

**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE**  
**ENGINEERING AND TECHNOLOGY**

**FABRICATION OF VANADIUM AND NIOBIUM BORIDES VIA  
MILLING-ASSISTED SOLID STATE SYNTHESIS METHODS  
AND SINTERING TECHNIQUES**

**Ph.D. THESIS**

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**Department of Metallurgical and Materials Engineering**

**Metallurgical and Materials Engineering Program**

**JULY 2015**



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**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

**VANADYUM VE NİYOBYUM BORÜRLERİN  
ÖĞÜTME DESTEKLİ KATI HAL SENTEZLEME YÖNTEMLERİ  
VE SİNERLEME TEKNİKLERİ İLE ÜRETİMİ**

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*To my dearest sister and  
to my family,*



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June 2015

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## ABBREVIATIONS

|                |                                                                 |
|----------------|-----------------------------------------------------------------|
| <b>Å</b>       | : Ångstrom                                                      |
| <b>AAS</b>     | : Atomic Absorption Spectrometer                                |
| <b>BET</b>     | : Brunauer-Emmett-Teller                                        |
| <b>BF</b>      | : Bright-Field                                                  |
| <b>BPR</b>     | : Ball-to-Powder Weight Ratio                                   |
| <b>BSE</b>     | : Back-Scattered Electron                                       |
| <b>CP</b>      | : Cold Pressing                                                 |
| <b>CVD</b>     | : Chemical Vapour Deposition                                    |
| <b>DC</b>      | : Direct Current                                                |
| <b>DSC</b>     | : Differential Scanning Calorimeter                             |
| <b>DSC/TG</b>  | : Differential Scanning Calorimeter/Thermogravimetry            |
| <b>DSC/TGA</b> | : Differential Scanning Calorimeter/ Thermogravimetric Analyser |
| <b>EDS</b>     | : Energy Dispersive Spectroscopy                                |
| <b>EDX</b>     | : Energy-Dispersive X-Ray Spectrometer                          |
| <b>emu</b>     | : Electromagnetic unit                                          |
| <b>eV</b>      | : Electron Volt                                                 |
| <b>FTIR</b>    | : Fourier Transform Infrared Spectroscopy                       |
| <b>g</b>       | : Gram                                                          |
| <b>h</b>       | : Hour                                                          |
| <b>HRTEM</b>   | : High Resolution TEM                                           |
| <b>HV</b>      | : Vickers Hardness                                              |
| <b>ICDD</b>    | : International Center for Diffraction Data <sup>®</sup>        |
| <b>kg</b>      | : Kilogram                                                      |
| <b>kJ</b>      | : Kilojoule                                                     |
| <b>l</b>       | : Liter                                                         |
| <b>M</b>       | : Molarity                                                      |
| <b>MA</b>      | : Mechanical Alloying                                           |
| <b>min</b>     | : Minute                                                        |
| <b>MO</b>      | : Metal Oxide                                                   |
| <b>µm</b>      | : Micrometer                                                    |
| <b>N</b>       | : Newton                                                        |
| <b>nm</b>      | : Nanometer                                                     |
| <b>Oe</b>      | : Oersted                                                       |
| <b>OM</b>      | : Optical Microscope                                            |
| <b>Pa</b>      | : Pascal                                                        |
| <b>PCA</b>     | : Process Control Agent                                         |
| <b>ppm</b>     | : Part per million                                              |
| <b>R</b>       | : Reductant                                                     |
| <b>PS</b>      | : Pressureless Sintering                                        |
| <b>PSA</b>     | : Particle Size Analyzer                                        |
| <b>RF</b>      | : Radio Frequency                                               |
| <b>rpm</b>     | : Rotation per minute                                           |
| <b>SADP</b>    | : Selected Area Diffraction Pattern                             |

|                      |                                               |
|----------------------|-----------------------------------------------|
| <b>SEM</b>           | : Scanning Electron Microscope                |
| <b>SHS</b>           | : Self-Propagating High-Temperature Synthesis |
| <b>SM</b>            | : Stereomicroscope                            |
| <b>SPS</b>           | : Spark Plasma Sintering                      |
| <b>TGA</b>           | : Thermogravimetric Analyser                  |
| <b>T<sub>M</sub></b> | : Melting Temperature                         |
| <b>TM</b>            | : Trademark                                   |
| <b>TEM</b>           | : Transmission Electron Microscope            |
| <b>V</b>             | : Volt                                        |
| <b>VSM</b>           | : Vibrating Sample Magnetometer               |
| <b>W</b>             | : Watt                                        |
| <b>XRD</b>           | : X-Ray Diffractometer                        |

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## LIST OF SYMBOLS

|                                    |                                     |
|------------------------------------|-------------------------------------|
| <b>a, b, c</b>                     | : Lattice parameters                |
| <b><math>\Delta G</math></b>       | : Gibbs free energy change          |
| <b><math>\Delta G^\circ</math></b> | : Standard Gibbs free energy change |
| <b><math>\Delta H</math></b>       | : Enthalpy change                   |
| <b><math>\Delta H_f</math></b>     | : Heat of formation                 |
| <b><math>K_{IC}</math></b>         | : Fracture toughness                |
| <b><math>\lambda</math></b>        | : Wavelength                        |
| <b>T</b>                           | : Temperature                       |
| <b><math>\theta</math></b>         | : Diffraction angle                 |
| <b><math>\sim</math></b>           | : Approximation                     |



# **FABRICATION OF VANADIUM AND NIOBIUM BORIDES VIA MILLING-ASSISTED SOLID STATE SYNTHESIS METHODS AND SINTERING TECHNIQUES**

## **SUMMARY**

The development of high technological boron products has attracted an increasing interest in the last half-century due to the demand for new materials having unique properties for special applications. Transition metal borides are the class of high-tech boron materials with attractive properties for diverse engineering applications where conventional materials cannot possess the rising requirements. The borides of vanadium and niobium have been characterized by the combination of high melting point, high hardness, high strength, good electrical and thermal conductivity, high chemical and thermal stability, low work function, good thermal shock resistance and corrosion resistance. This combination of excellent properties permits their applications in many areas such as mechanical industry, chemistry and microelectronic fields. They are recognized as the candidates for high-temperature structural applications including surface and thermal protection, refractory crucibles and plasma arc electrodes. Vanadium borides as coating materials on various steels and as wear resistant materials have been reported in many studies. Vanadium borides are promising for use as the anode material for air batteries due to their exceptionally high discharge capacity. Niobium borides are known as refractory coating materials that have excellent oxidation stability at high temperatures. It was also reported as an electrode for use in the refining of aluminium and as a current-conducting element in contact with molten aluminium in electrolytic cells. Non-stoichiometric compounds of niobium boride have been discussed in many reports as potential superconductors.

Many production techniques have been applied in the preparation of vanadium and niobium borides. They have been fabricated conventionally by high temperature methods such as borothermal/carbothermal reduction processes, direct solid-phase reactions, arc melting or chemical vapour deposition. The recent techniques developed for preparing vanadium and niobium borides are self-propagating high-temperature synthesis (SHS), low-temperature synthesis in an autoclave and ball milling and mechanochemical synthesis. Even though many studies are available for the fabrication of vanadium and niobium boride powders, sintering processes of them have not been a well discussed topic in the literature. Recent studies are mainly focused on the sintering of niobium borides using various techniques including high pressure sintering and spark plasma sintering, however, these studies have been mostly carried out in order to investigate superconducting behaviour of niobium borides. Only a few studies reported the consolidation behaviour and mechanical properties of the sintered vanadium and niobium boride and their composites. However, it is significant to improve an effective fabrication technique of the sintered boride bodies and to investigate their consolidation behaviour and

mechanical properties for determining their application areas. On the other hand, the use of high temperatures, expensive starting materials (elemental V/Nb or B) and/or complicated equipment may restrict the fabrication process to obtain vanadium and niobium borides for the demanded applications. Conventional techniques have some general restrictions such as high temperature operation, the formation of by-products and grain growth during processing.

One of the major aims of this dissertation is to find an effective technique for preparing metal borides that could overcome the limitations of conventional productions and represent the advantages of time and energy savings, simplicity, low-cost raw materials and high-purity products. Milling-assisted solid-state methods utilized in this dissertation involve inducing chemical reactions in powder blends at room temperature or lower temperatures than thermodynamically required. The primary purpose of this dissertation is the preparation of vanadium and niobium boride and niobium boride-based composite powders in high-purity through economical ways from their oxide raw materials ( $V_2O_5$ ,  $Nb_2O_5$ ) and native boron source ( $B_2O_3$ ) in presence of reducing agents (Mg, C). The powder preparations were utilized using two different techniques including mechanochemical reactions using oxide raw materials/Mg reductant and milling-assisted carbothermal reactions using oxide raw materials/C reductant. The consolidation of the obtained powders by different techniques was also intended in order to investigate the sintering behaviours, microstructural and mechanical properties of the final samples. In overall, detailed characterization investigations of the obtained boride and boride-based powders and their sintered products were carried out by means of various analysis techniques.

Firstly, the fabrication of vanadium boride powders was investigated through the mechanochemical reactions of  $V_2O_5$ - $B_2O_3$ -Mg powder blends in terms of varying milling times and  $B_2O_3$  or Mg contents. Nano-sized vanadium boride powders having  $VB_2$ - $VB$ - $V_3B_4$  phases were obtained in high purity without any intermediate phase and any impurity. Secondly, the fabrication of niobium boride powders was investigated through the mechanochemical reactions of  $Nb_2O_5$ - $B_2O_3$ -Mg powder blends in terms of varying milling times, considering thermal behaviours and applying an additional annealing process. Niobium boride powders having  $NbB$ ,  $NbB_2$  and  $Nb_3B_4$  phases in various amounts and single phase  $NbB$  powders were successfully synthesized with high-purity and nano-size. Thirdly, the fabrication of niobium boride-niobium carbide composite powders was investigated by mechanical milling of  $Nb_2O_5$ - $B_2O_3$ -C powder blends and subsequent annealing processes in terms of varying milling times, annealing temperature and C content.  $NbB_2$ -based composite powders comprising various amounts of  $NbC$  were fabricated via a carbothermal route in high-purity at reduced temperatures due to the effect of mechanical milling of stoichiometric powder blends. Finally, sintering of the obtained vanadium and niobium boride powders in high qualities was carried out by cold pressing/pressureless sintering (without or with metallic Co addition) and spark plasma sintering (SPS) techniques. The results were discussed regarding the effect of different production conditions and sintering techniques on the consolidation behaviour, microstructure and mechanical properties of the bulk samples. Bulk vanadium boride and niobium boride products fabricated by SPS and bulk niobium boride products fabricated by activated pressureless sintering exhibited high density, high hardness, high wear resistance and high friction coefficients. Furthermore, high

elastic modulus and high fracture toughness values were obtained for the samples fabricated by activated pressureless sintering.

This dissertation work contributed the first results to the literature on the preparation of pure vanadium and niobium boride powders via mechanochemical route of oxide starting materials. This work also revealed the first scientific data on the *in-situ* formation of NbB<sub>2</sub>-NbC composite powders via milling-assisted carbothermal route from oxide starting materials at decreased temperatures due to the effect of mechanical milling. Furthermore, the consolidation and characterization studies of the sintered vanadium and niobium borides also contributed to the literature in terms of sintering behaviour and mechanical properties. In conclusion, the significant outputs of this dissertation were obtaining the high-technology boron products from low-cost raw materials and creating of added value by using the native boron sources.



# **VANADYUM VE NİYOBYUM BORÜRLERİN ÖĞÜTME DESTEKLİ KATI HAL SENTEZLEME YÖNTEMLERİ VE SİNERLEME TEKNİKLERİ İLE ÜRETİMİ**

## **ÖZET**

Özgün özelliklere sahip yeni malzemelere özel uygulama alanlarında duyulan ihtiyaç, ileri teknoloji bor ürünlerinin geliştirilmesi üzerine yapılan çalışmaların özellikle geçtiğimiz son yarım yüzyılda artan bir ilgi görmesine neden olmuştur. Geçiş metal borürleri, sahip oldukları üstün özellikler ile ileri teknoloji bor ürünleri sınıflandırılmasında olup, farklı ve uç mühendislik uygulamalarında geleneksel malzemelerin karşılayamadığı ihtiyaçlar için alternatif malzemeler olarak konumlandırılmaktadır. Bu malzemeler arasında vanadyum ve niyobyum borürler, yüksek ergime noktası, yüksek sertlik, yüksek dayanım, iyi elektriksel ve termal iletkenlik, yüksek kimyasal ve termal kararlılık, düşük elektronik iş fonksiyonu, iyi termal şok direnci ve korozyon direnci ile karakterize edilirler. Tüm bu üstün özelliklerin birleşimi, bu malzemelerin mekanik endüstrisi, kimya ve mikroelektronik alanlarında kullanımına olanak sağlar. Yüzey ve termal koruma gerektiren alanlar, refrakter potalar ve plazma ark elektrotları olmak üzere birçok yüksek sıcaklık uygulamalarında kullanıma aday gösterilirler. Vanadyum borürlerin, çeliklerde kaplama ve aşınmaya dirençli malzeme olarak kullanıldığı birçok çalışma mevcuttur. Ayrıca vanadyum borürler, sahip oldukları oldukça yüksek deşarj kapasiteleri sayesinde, hava pilleri için alternatif anot malzemesidir. Niyobyum borürler, oldukça iyi oksidasyon dirençleri sayesinde refrakter kaplama malzemesi olarak kullanılmaktadır. Ayrıca alüminyumun saflaştırılmasında kullanılmakta ve alüminyum elektrolizinde kaplama malzemesi olarak kullanıma aday gösterilmektedir. Niyobyum borürün stokiometrik olmayan bileşikler, şu ana kadar yapılan birçok bilimsel çalışmada potansiyel bir süper iletken malzeme olarak tanımlanmıştır.

Vanadyum ve niyobyum borürlerin üretimine yönelik yapılmış birçok çalışma mevcuttur. Geleneksel olarak yüksek sıcaklıkta direkt katı-faz reaksiyonu, borotermal/karbotermal redüksiyon prosesleri, ark ergitme veya kimyasal buhar biriktirme yöntemleri ile üretilirler. Kendiliğinden ilerleyen yüksek sıcaklık sentezi, düşük sıcaklıkta otoklavda sentez ve mekanik öğütme/mekanokimyasal sentezleme yöntemleri, vanadyum ve niyobyum borürlerin üretimine yönelik son dönemlerde geliştirilmiş yeni yöntemlerdendir. Vanadyum ve niyobyum borür tozlarının üretimine yönelik geliştirilmiş birçok metot olmasına rağmen, söz konusu borürlerin sinterleme prosesi literatürde detaylı olarak incelenmemiştir. Yapılan son çalışmalar, niyobyum borürlerin yüksek basınç ve spark plazma sinterleme yöntemleri yığın yapıya getirilmesine odaklanmış olup, çoğu süper iletkenlik davranışlarını incelemeye yöneliktir. Literatürdeki çok kısıtlı sayıdaki çalışma, vanadyum ve niyobyum borürlerin sinterleme davranışlarını ve mekanik özelliklerini incelemektedir. Ancak söz konusu borürlerin kullanım alanlarının belirlenmesinde, sinter ürünlerinin geliştirilmesi ve mekanik özelliklerinin incelenmesi çok önemli bir

role sahiptir. Öte yandan, vanadyum ve niyobyum borürlerin üretiminde kullanılan yüksek sıcaklık koşulları, oldukça pahalı hammaddeler (elementer V/Nb, B) ve/veya karmaşık makine/teçhizatlar, ihtiyaç bulunan alanlarda kullanımını kısıtlamaktadır. Geleneksel yöntemlerin, yüksek sıcaklık uygulama koşulları, proses sırasında istenmeyen yan ürünlerin oluşumu ve tane büyümesi gibi son ürün özelliklerini etkileyen negatif yönleri bulunmaktadır.

Bu tez çalışmasının en önemli amaçlarından biri, metal borürlerin üretiminde geleneksel yöntemlerin dezavantajlarını ortadan kaldıran; zaman ve enerji tasarrufu sağlayan, basitlik içeren, düşük maliyetli hammaddelerin kullanıldığı ve yüksek safiyette tozların elde edildiği verimli üretim yöntemlerinin araştırılmasıdır. Bu tez çalışmasında, oda sıcaklığında ya da termodinamik olarak gereken sıcaklığın altındaki düşük sıcaklıklarda gerçekleştirilen öğütme destekli katı hal sentezleme yöntemleri kullanılmıştır. Bu tez çalışmasının öncelikli amacı, vanadyum ve niyobyum borür tozlarının ve niyobyum borür esaslı kompozit tozların, oksit hammaddeleri ( $V_2O_5$ ,  $Nb_2O_5$ ) ve yerli bor kaynağı ( $B_2O_3$ ) kullanılarak, redükleyici ajanlar yardımıyla (Mg, C) ekonomik yollardan yüksek safiyette eldesidir. Toz üretimi, oksit hammaddeler/Mg redükleyici ajanı kullanılarak mekanokimyasal reaksiyonlar ve oksit hammaddeler/C redükleyici ajanı kullanılarak karbotermal reaksiyonlar olmak üzere iki farklı yöntem ile gerçekleştirilmiştir. Elde edilen tozlar, sinterleme davranışlarının belirlenmesi, mikroyapı ve mekanik özelliklerinin incelenmesi amacıyla farklı yöntemler ile sinterlenmiştir. Tez çalışmasının bütününde, elde edilen tozların ve yığın yapıdaki ürünlerin ayrıntılı karakterizasyon çalışmaları çeşitli yöntemler yardımıyla yapılmıştır.

İlk aşamada, vanadyum borür tozlarının üretimi için,  $V_2O_5$ - $B_2O_3$ -Mg toz karışımlarının mekanokimyasal reaksiyonları, değişen öğütme süreleri ve değişen  $B_2O_3$  ya da Mg miktarları göz önüne alınarak incelenmiştir. Nano boyutta VB<sub>2</sub>-VB-V<sub>3</sub>B<sub>4</sub> fazlarını içeren vanadyum borür tozları hiçbir ara faz ya da empürite içermeyen yüksek safiyette elde edilmiştir. İkinci aşamada, niyobyum borür tozlarının üretimi için,  $Nb_2O_5$ - $B_2O_3$ -Mg toz karışımlarının mekanokimyasal reaksiyonları, değişen öğütme süreleri, tozların termal davranışları ve uygulanan ek tavlama prosesi göz önüne alınarak incelenmiştir. Nano boyutta NbB<sub>2</sub>-NbB-Nb<sub>3</sub>B<sub>4</sub> fazlarını içeren niyobyum borür tozları ve tek faz NbB tozları yüksek safiyette elde edilmiştir. Üçüncü aşamada, niyobyum borür-niyobyum karbür tozlarının üretimi için,  $Nb_2O_5$ - $B_2O_3$ -C toz karışımlarının mekanik öğütme ve takip eden tavlama prosesleri, değişen öğütme süreleri, değişen tavlama sıcaklıkları ve değişen C miktarı göz önüne alınarak incelenmiştir. Farklı miktarlarda NbC içeren NbB<sub>2</sub> esaslı kompozit tozlar, karbotermal yöntem ile mekanik öğütme sayesinde düşürülmüş sıcaklıklarda ve yüksek safiyette elde edilmiştir. Son olarak, yüksek kalitede elde edilen vanadyum ve niyobyum borür tozları, soğuk presleme/basınçsız sinterleme (katkısız ya da metalik Co katkısı ile) ve spark plazma sinterleme yöntemleri ile yığın yapıya getirilmiştir. Sinter sonuçları, farklı toz üretim metotlarının ve sinterleme tekniklerinin son malzemelerin mikroyapı ve mekanik özellikleri üzerindeki katkısı göz önüne alınarak incelenmiştir. Spark plazma sinterleme ile elde edilen yığın yapıdaki niyobyum ve vanadyum borürler ve Co aktive edilmiş basınçsız sinterleme yoluyla elde edilen niyobyum borürler, yüksek yoğunluk, yüksek sertlik, yüksek aşınma direnci ve yüksek sürtünme katsayısı değerleri vermiştir. Ayrıca, oldukça yüksek elastisite modülü ve tokluk değerleri, Co aktive edilmiş basınçsız sinterleme yoluyla elde edilmiştir.

Bu tez çalışması, saf vanadyum ve niyobyum borür tozlarının mekanokimyasal yöntemler ile oksit hammaddelerden hareketle elde edilmesine yönelik literatürdeki önemli bir açığı kapatmaktadır. Ayrıca bu tez çalışmasında uygulanan öğütme destekli karbotermal süreçler ile saf NbB<sub>2</sub>-NbC tozlarının oksit hammaddelerden *in-situ* eldesi, literatürdeki ilk bilimsel bilgileri oluşturmaktadır. Tüm bunların yanında, vanadyum ve niyobyum borürlerin sinterleme çalışmaları ve elde edilen mikro yapısal ve mekanik özellikler literatüre önemli bir katkıda bulunmaktadır. Sonuç olarak, düşük maliyetli oksit hammaddelerden hareketle elde edilen ileri teknoloji bor ürünleri ve yerli bor malzemesi kullanımından kaynaklı yaratılan katma değer, bu tez çalışmasının en önemli çıktılarından biridir.



## 1. INTRODUCTION

High-tech boron materials are interesting candidates for industry for diverse engineering applications where conventional materials cannot meet the rising requirements. Transition metal borides have been attracted great attention with their attractive properties for years. The borides of VB group transition metals (V, Nb and Ta) have a unique combination of high hardness, high strength, good electrical and thermal conductivity, low work function, high chemical stability as well as good thermal shock resistance and corrosion resistance (Yao et al, 2012). This combination of excellent properties enables their applications in surface and thermal protection, cutting tools, refractory crucibles, impact-resistant armours and plasma arc electrodes (Gidikova, 2000; Sen, 2005; Usta, 2005; Tarakci et al, 2010; Yao et al, 2012). There are six vanadium borides ( $V_3B_2$ , VB,  $V_5B_6$ ,  $V_3B_4$ ,  $V_2B_3$ , and  $VB_2$ ) and five niobium borides ( $Nb_3B_2$ , NbB,  $Nb_5B_6$ ,  $Nb_3B_4$ , and  $NbB_2$ ) that have been experimentally reported and structurally well-determined in the V–B and Nb–B systems, respectively (Rudy and Windisch, 1966; Massalski, 1990; Nunes et al, 2004; Yeh and Chen, 2006a; Okamoto, 2008; Yeh and Wang, 2011; Yao et al, 2012).

Vanadium borides have been used as high-temperature materials, surface protection components and wear resistant materials due to their attractive properties (Gidikova, 2000; Zhou et al, 2009; Tarakci et al, 2010; Yeh and Wang, 2011). Vanadium borides as coating materials on various steels have been reported in many studies (Gidikova, 2000; Sen, 2005).  $VB_2$  has been suggested as alloying addition for the high speed steels which has been used as materials for cutting tools (Ebner et al, 1996). Vanadium boride powders have been also used as dispersion agent in iron-based alloy matrix and as strengthening phases of composition coatings (Saito and Tanaka, 1998; Rudneva and Galevskii, 2007). In addition to that, vanadium borides are promising for use as the anode material for air batteries due to their exceptionally high discharge capacity.  $VB_2$  air cell energy capacity is several times higher than that of gasoline, hydrogen, conventional Zn anode and also all rechargeable batteries including Li ion, metal hydride or lead acid (Licht et al, 2008; Wang et al, 2010; Wang et al, 2012; Licht et al, 2012). Niobium borides have received a great deal of

attention owing to their applications in mechanical industry, chemistry and microelectronics fields (Torabi et al, 2015). Especially the compound,  $\text{NbB}_2$ , is recognized as the potential candidate for high temperature structural applications (Ma et al, 2009). Niobium borides are known as a refractory and a coating material which has excellent oxidation stability at high temperatures (Motojima et al, 1975). It has been also reported that niobium borides are suitable as coatings for high-current hot cathodes due to their resistant to high temperatures and low work functions (Url-2).  $\text{NbB}_2$  has been reported as an electrode for use in the refining of aluminium (Murata, 1971). Non-stoichiometric compounds of niobium diboride have been a matter in many reports as potential superconductors (Shein and Ivanovskii, 2002; Yamamoto et al, 2002; Joseph et al, 2003; Ren et al, 2008; Mudgel et al, 2008). Nb-deficient diborides in  $\text{NbB}_2$  showed superconductivity with a transition up to 11 K which makes to use it as superconducting material (Mudgel et al, 2008).

Many production techniques have been applied in the preparation of vanadium and niobium borides. Various stoichiometries of these borides have been fabricated conventionally by high temperature methods such as borothermal/carbothermal reduction processes, direct solid-phase reactions or arc melting (Peshev et al, 1968; Peshev et al, 1968; Matsumoto et al, 1982; Jha et al, 2011; Yu and Lundström, 1995; Bulfon et al, 1997; Nunes et al, 2004; Junior et al, 2003; Takahashi et al, 2005; Nunes et al, 2005; Makarenko et al, 1998; Maeda et al, 1994; Okada et al, 2008; Matsudaira et al, 1989; Cheng et al, 2013). Another traditional technique to synthesize diborides of niobium is chemical vapour deposition using gas mixtures (Motojima et al, 1975). In order to obtain single crystals of vanadium and niobium diborides, floating zone method has been also applied using  $\text{VB}_2$  and  $\text{NbB}_2$  starting materials (Nakano et al, 1981; Otani et al, 1998). The recent techniques developed for preparing vanadium and niobium borides are self-propagating high-temperature synthesis (SHS) (Yeh and Wang, 2011; Takeya et al, 2004; Tsuchida and Kakuta, 2005; Yeh and Chen, 2006a; Yeh and Chen, 2006b; Tsuchida and Kakuta, 2007; Yeh and Wang, 2010), low-temperature synthesis in an autoclave (Shi et al, 2004; Cai et al, 2005; Ma et al, 2009) and ball milling and mechanochemical synthesis (Kim et al, 2008; Wang et al, 2010; Licht et al, 2012; Morris and Morris, 1991; Iizumi et al, 2006; Torabi et al, 2015; Jafari et al, 2015).

The application of high temperatures, the use of expensive starting materials (elemental V/Nb or B) and/or the use of complicated equipment may restrict the fabrication process to obtain vanadium and niobium borides for the demanded applications. Conventional techniques have some general restrictions such as high temperature operation, the formation of by-products and grain growth during processing. Thus, it is necessary to find an effective technique that could overcome these limitations and represent the advantages of time and energy savings, simplicity and high-purity products. Furthermore, considering the control over the microstructure (shape, size etc.) and the refinement of the resultant products is essential for many application areas.

Few studies exist in the literature relating the consolidation of vanadium and niobium borides. Recent studies are mainly focused on the sintering of niobium borides using various techniques including high pressure sintering and spark plasma sintering (SPS) of elemental Nb and B powder mixtures (Matsudaira et al, 1989; Yamamoto et al, 2002; Sairam et al, 2014) and pressureless sintering using NbB<sub>2</sub>/B/Nb starting materials (Mudgel et al, 2008; Ren et al, 2008). Sintering studies have been mostly carried out in order to investigate superconducting behaviour of niobium borides (Yamamoto et al, 2002; Mudgel et al, 2008; Ren et al, 2008). Only few studies reported the mechanical properties (i.e. microhardness, fracture toughness, elastic modulus) of the sintered niobium boride bodies (Matsudaira et al, 1989 and Sairam et al, 2014). However, it is significant to improve an effective fabrication technique of the sintered boride bodies and to investigate their consolidation behaviour and mechanical properties for determining their application areas.

In this dissertation, different milling-assisted solid state synthesis methods and different sintering techniques will be utilized to fabricate vanadium and niobium boride powders and their sintered bodies. The primary purpose of this dissertation is the preparation of boride and boride-based composite powders in high-purity through economical ways from their oxide raw materials (V<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>) and native boron source (B<sub>2</sub>O<sub>3</sub>) in presence of reducing agents (Mg, C). The consolidation of the obtained powders is also another aim in order to investigate the sintering behaviours, microstructural and mechanical properties of the final samples. The other purpose is to generate a thermodynamic description of the applied systems and to predict the reaction mechanisms. For this purpose, thermodynamic calculations will be done by

FactSage<sup>TM</sup> software and compared to the phase detections and thermal analyses. Detailed characterization investigations of the obtained boride and boride-based powders and sintered products will be carried out by means of various analysis techniques.

Firstly, the fabrication of vanadium boride powders will be investigated through the mechanochemical reactions of  $V_2O_5$ - $B_2O_3$ -Mg powder blends in terms of varying milling times and  $B_2O_3$  or Mg contents. Secondly, the fabrication of niobium boride powders will be investigated through the mechanochemical reactions of  $Nb_2O_5$ - $B_2O_3$ -Mg powder blends in terms of varying milling times, considering thermal behaviours and applying an additional annealing process. Thirdly, the fabrication of niobium boride-niobium carbide composite powders will be investigated by mechanical milling of  $Nb_2O_5$ - $B_2O_3$ -C powder blends and subsequent annealing process in terms of varying milling time, annealing temperature and C content. The characterization of the obtained boride and boride-based powders will be performed by using XRD, DSC/TG, SM, SEM/EDX, TEM analyses and particle size, density and magnetic measurements. Finally, sintering of the obtained vanadium and niobium boride powders in high qualities will be carried out by cold pressing/pressureless sintering (with or without metallic Co addition) and spark plasma sintering (SPS) techniques. The results will be discussed regarding the effect of different production conditions and sintering methods on the consolidation behaviour, microstructure and mechanical properties of the bulk samples. The consolidation behaviour and microstructural characterization of the sintered samples will be conducted by XRD, SEM, OM techniques and density measurements. Mechanical properties of the bulk products will be described in terms of microhardness, wear characteristics, elastic modulus, indentation behaviour and fracture toughness.

## **2. LITERATURE REVIEW**

Literature review of this dissertation comprises the general properties and application areas and production/sintering techniques of vanadium and niobium borides, general information about mechanical alloying and milling-assisted methods and detailed description of mechanochemical synthesis and mechanically activated annealing processes which were used as ball-milling assisted solid state methods in the scope of this dissertation.

### **2.1 Vanadium and Niobium Borides**

The borides of VB group transition metals (V, Nb and Ta) have a unique combination of high hardness, electrical and thermal conductivities, chemical stability as well as good thermal shock resistance and corrosion resistance (Yao et al, 2012). This combination of excellent properties permits their applications in surface and thermal protection, cutting tools, refractory crucibles, impact-resistant armours and plasma arc electrodes (Gidikova, 2000; Sen, 2005; Usta, 2005; Tarakci et al, 2010; Yao et al, 2012). There are six vanadium borides ( $V_3B_2$ , VB,  $V_5B_6$ ,  $V_3B_4$ ,  $V_2B_3$ , and  $VB_2$ ) and five niobium borides ( $Nb_3B_2$ , NbB,  $Nb_5B_6$ ,  $Nb_3B_4$ , and  $NbB_2$ ) that have been experimentally reported and structurally well-determined in the V–B and Nb–B systems, respectively (Rudy and Windisch, 1966; Massalski, 1990; Nunes et al, 2004; Yeh and Chen, 2006a; Okamoto, 2008; Yeh and Wang, 2011; Yao et al, 2012).

#### **2.1.1 Properties and application areas of vanadium borides**

Vanadium borides, like other borides of transition metals, are well known for its high melting point, high strength, high chemical stability and good wear resistance (Bulfon et al, 1997; Erdemir et al, 1997; Ivanovsky et al, 1998; Zhou et al, 2009). The cohesive properties and chemical stability for hexagonal diborides of IVA and VA group metals ( $MB_2$ ) were analysed by using the results of full-potential LMTO calculations (Ivanovsky et al, 1998). A comparison of covalent boron-metal interactions in  $MB_2$  phases showed that  $NbB_2$  and  $VB_2$  have the highest chemical

stabilities among the analysed transition metal borides (Ivanovsky et al, 1998). Figure 2.1(a)-(b) show the binary phase diagrams of the V-B system proposed by Rudy and Windisch (1966) and Massalski (1990). They present six stable stoichiometric borides:  $V_3B_2$ , VB,  $V_5B_6$ ,  $V_3B_4$ ,  $V_2B_3$ ,  $VB_2$ . The main differences between two diagrams are related to the melting points of the boride phases. As seen from Figure 2.1(a) and (b), vanadium borides form from the liquid through peritectic ( $V_3B_2$ , VB,  $V_3B_4$  and  $V_2B_3$ ) and congruent ( $VB_2$ ) reactions, whereas only  $V_5B_6$  phase has peritectoid formation.

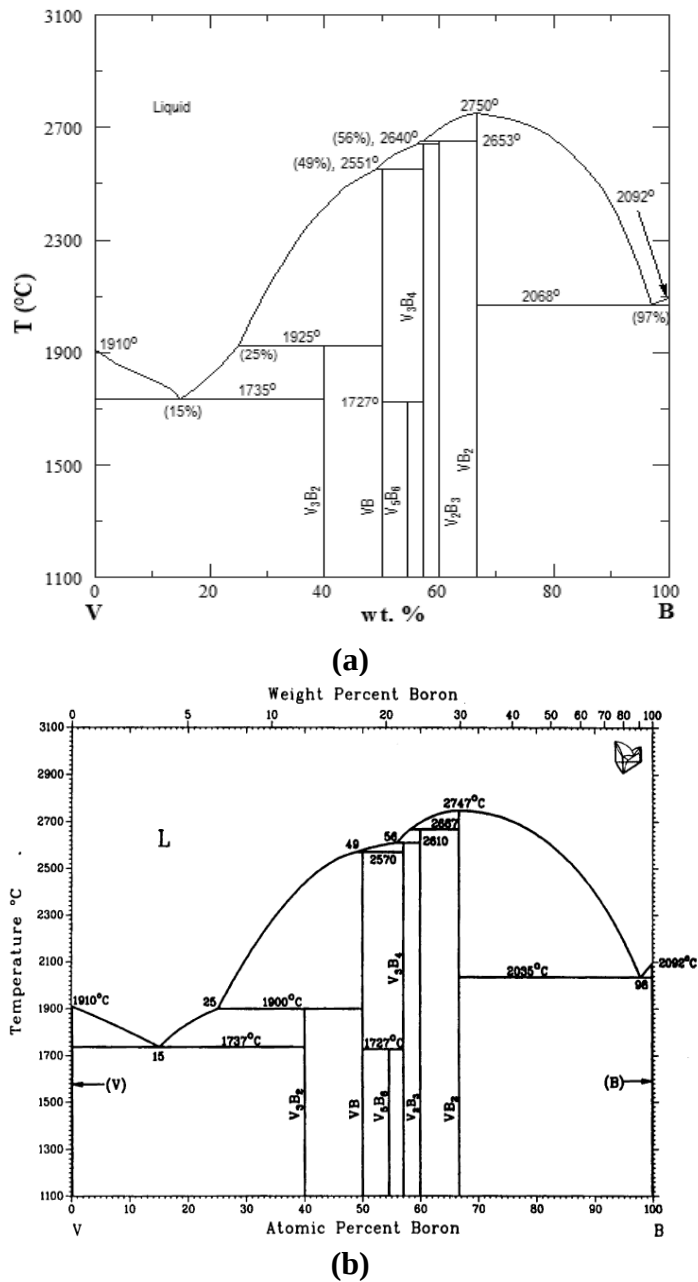


**Figure 2.1** : Binary phase diagrams of the V-B system proposed by (a) Rudy and Windisch (1966) and (b) Massalski (1990).

Among the all vanadium boride phases,  $\text{VB}_2$  is the most stable one which has a melting point of  $\sim 2750^\circ\text{C}$ . Therefore, the boride phase of  $\text{VB}_2$  has been mostly studied in the current literature up to now. On the one hand, there is some studies about the stability of  $\text{V}_5\text{B}_6$  phase (Nunes et al, 2004),  $\text{V}_2\text{B}_3$  phase (Okada et al, 2008) and other phases (Yeh et al, 2011).

Ball-and-stick model for the crystal structures of  $\text{VB}_2$  is shown in Figure 2.2, adapted from Zhou et al (2009).  $\text{VB}_2$  belongs to the hexagonal  $\text{AlB}_2$  structure with the space group  $\text{P6}/\text{mmm}$ . There are three atoms in the unit cell, all of them on the special positions: V atom at the origin and two B atoms at the site. The structure is extremely simple in that it is defined by two lattice parameters of  $a$  and  $c$  and has a very small unit cell (Zhou et al, 2009).

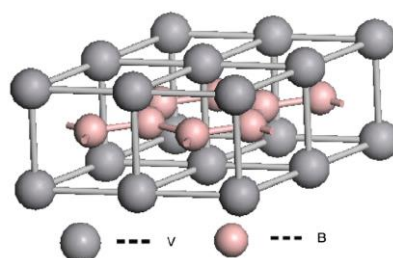


**Figure 2.2 :** The crystal structure of  $\text{VB}_2$  adapted from Zhou et al (2009).

Yao et al (2012) employed the theoretical first-principle total energy calculations on VB group transition metal borides with various stoichiometries ( $\text{M}_2\text{B}$ ,  $\text{M}_3\text{B}_2$ ,  $\text{MB}$ ,  $\text{M}_5\text{B}_6$ ,  $\text{M}_3\text{B}_4$ ,  $\text{M}_2\text{B}_3$ , and  $\text{MB}_2$ ). Results showed that all these borides are thermodynamically and mechanically stable. Among the borides,  $\text{MB}_2$  has relatively high stability because of more negative value of calculated heat of formation ( $\Delta H_f$ ). With the increasing boron concentration, the obtained  $\Delta H_f$  curves both for the V-B and Nb-B systems show a similar decreasing tendency which indicates that the phases with higher boron contents might be easier to be synthesized in experiments than that of lower ones. Furthermore,  $\Delta H_f$  values of vanadium boride phases are more negative than that of niobium boride phases, implying vanadium borides may be easier to be obtained than niobium borides through solid state reaction of constituent elements.

As an example of the structural features of the studied borides, the optimized crystal structures of V-B systems were modelled (Figure 2.3). In VB structure, the distance between B atoms and the covalent V-B bonding length are shorter than that of  $\text{V}_3\text{B}_2$

and  $V_2B$ , indicating its relatively stronger B–B bonding. These shortened B–B and V–B interactions for VB may give rise to the relatively higher mechanical performance of VB (Yao et al, 2012).

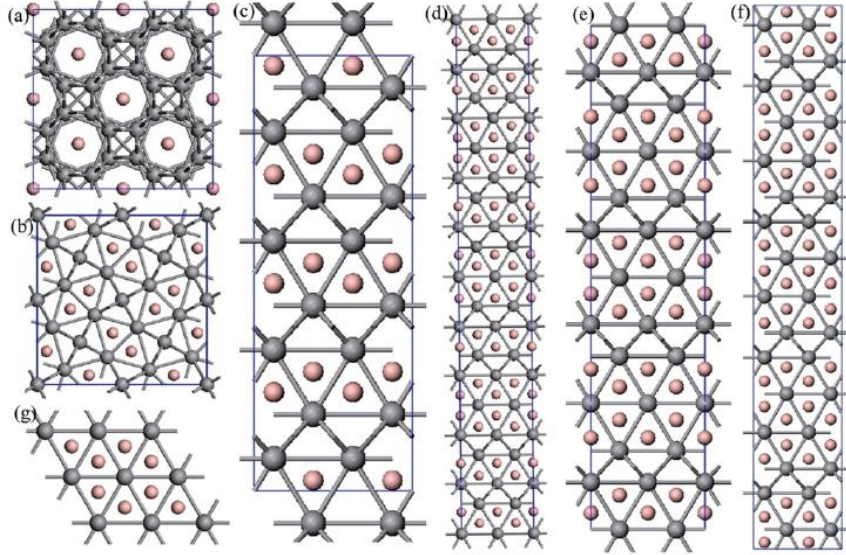


**Figure 2.3 :** The optimized crystal structures of (a)  $V_2B$ , (b)  $V_3B_2$ , (c) VB, (d)  $V_5B_6$ , (e)  $V_3B_4$ , (f)  $V_2B_3$ , and (g)  $VB_2$ , adapted from Yao et al (2012).

Bulfinch et al (1997) measured a Vickers microhardness of  $HV_{0.02} = 30.6$  GPa of  $VB_2$  single crystals prepared by arc melting of pellets of V ingots and B powders. Zhou et al (2009) calculated the hardness of  $VB_2$  as  $HV = 26.6$  GPa according to a quantitative theoretical prediction model for hardness calculation from V-B bond by using Mulliken population. Tarakci et al (2010) reported the microhardness of the  $VB_2$  layer, obtained by pack boronizing of pure vanadium at  $1100^\circ\text{C}$  for 4, 8, 12 and 16 h, as approximately 3700 HV for all boriding times. Moreover, the fracture toughness of the boride layer was calculated using Vickers indentations with cracks through Palmqvist and median/radial approaches, which gave the values of 2.1-5.9 and 1.7-3.4  $\text{MPa}\cdot\text{m}^{1/2}$ , respectively (Tarakci et al, 2010). Gidikova et al (2000) reported the vanadium boride coatings on steel by boronizing at  $950$ - $1000^\circ\text{C}$  for 5 and 9 h and surface zone consisted of  $VB_2$  had a microhardness of 23.6 GPa.

Table 2.1 summarizes the general properties of three vanadium boride phases obtained from both experimental and theoretical studies. A study about the theoretical investigation on the transition-metal borides with  $Ta_3B_4$ -type structure showed that  $V_3B_4$  exhibited the highest Young's modulus (555 GPa) and microhardness (26.4 GPa) values among the  $Ta_3B_4$ -type structure of IVB, VB and

VIB group transition metal borides (Miao et al, 2011). The thermal expansion coefficient of  $\text{VB}_2$  ( $7.6 \times 10^{-6}/^\circ\text{C}$ ) is much higher than those of IVB group transition metal borides ( $4.6\text{-}6.3 \times 10^{-6}/^\circ\text{C}$ ) (Samsonov and Kovenskaya, 1977). Yao et al (2012) investigated the mechanical and electronic properties of VB group transition metal borides with different boron concentrations ( $\text{M}_2\text{B}$ ,  $\text{M}_3\text{B}_2$ ,  $\text{MB}$ ,  $\text{M}_5\text{B}_6$ ,  $\text{M}_3\text{B}_4$ ,  $\text{M}_2\text{B}_3$ , and  $\text{MB}_2$ ). Thermodynamic stability and bulk modulus of V and Nb borides presented an increasing trend with the increase of boron concentrations (Yao et al, 2012). As shown in Table 2.1, vanadium borides have high melting points ( $2551\text{-}2750^\circ\text{C}$ ) and high strengths ( $526\text{-}563$  GPa). In addition, an investigation on the thermal oxidation resistance of refractory carbides and borides showed that the onset oxidation temperature of  $\text{VB}_2$  nanopowders in air was found as  $\sim 350^\circ\text{C}$  (Rudneva and Galevskii, 2007).

**Table 2.1 :** General properties of vanadium borides, adapted from Aronsson (1964), Rudy and Windisch (1966), Goldschmidt (1967), Samsonov and Kovenskaya (1977), Massalski (1990), Bulfon et al (1997), Miao et al (2011), Yao et al (2012), Qi et al (2014), Url-1.

| Properties                                                 | $\text{VB}_2$ | VB                 | $\text{V}_3\text{B}_4$ |
|------------------------------------------------------------|---------------|--------------------|------------------------|
| Structure                                                  | Hexagonal     | Orthorhombic       | Orthorhombic           |
| Theoretical density ( $\text{g}/\text{cm}^3$ )             | 5.01          | 5.63               | 5.46                   |
| Melting point ( $^\circ\text{C}$ )                         | $\sim 2750$   | $2551\text{-}2570$ | $2610\text{-}2640$     |
| Electrical resistivity ( $\mu\Omega\cdot\text{cm}$ )       | 16-38         | 35-40              | 16                     |
| Thermal conductivity ( $\text{W}/\text{cm}\cdot\text{K}$ ) | 0.42          | -                  | -                      |
| Thermal expansion coefficient ( $10^{-6}/^\circ\text{C}$ ) | 7.6           | -                  | -                      |
| Work function (eV)                                         | 3.88          | -                  | -                      |
| Hardness (GPa)                                             | 20.3-36.8     | 22.8-34.2          | 23-38.1                |
| Young's modulus (GPa)                                      | 556-563       | 526                | 547-555                |

Due to their attractive properties, vanadium borides have promising applications in many areas. They have been used as high-temperature materials, surface protection components and wear resistant materials (Gidikova, 2000; Zhou et al, 2009; Tarakci et al, 2010; Yeh and Wang, 2011). Vanadium borides as coating materials on various steels have been reported in many studies (Gidikova, 2000; Sen, 2005).  $\text{VB}_2$  has been suggested as alloying addition for the high speed steels which has been used as materials for cutting tools (Ebner et al, 1996). It was reported that the addition of vanadium boride and vanadium carbide increased the amount of hard intermetallic phases in the laser alloyed tracks on high speed steel substrates (Ebner et al, 1996). Vanadium boride powders have been also used as dispersion agent in an iron-based

alloy matrix and iron-based sintered bodies dispersed with boride particles showed a significant improvement on strength and toughness values compared to those of conventional ones (Saito and Tanaka, 1998). Furthermore,  $\text{VB}_2$  nanopowders have been recommended for use as strengthening phases of composition coatings that operate in oxidizing media at temperatures not higher than  $\sim 350^\circ\text{C}$  (Rudneva and Galevskii, 2007).

A computational thermodynamic study on the stability of  $\text{V}_3\text{B}_4$  suggested that it was stable enough as a refractory material for high temperature composite applications (Wiedemeier and Singh, 1991). In addition to that vanadium borides are promising for use as the anode material for air batteries due to their exceptionally high discharge capacity (Licht et al, 2008; Wang et al, 2010; Wang et al, 2012; Licht et al, 2012).

Wang et al (2010) characterized the electrochemical discharge performances of the  $\text{VB}_x$  alloys as anodic materials for air batteries. The introduction of small amount of B into V caused a dramatic improvement in the anodic activity of elemental V, showing strong discharge capability. All the prepared  $\text{VB}_x$  anodes in this study delivered an extraordinary capacity of  $>2000 \text{ mAh g}^{-1}$  (Wang et al, 2010).

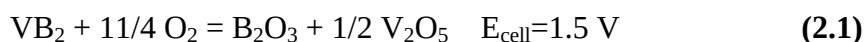
In another study regarding the synthesis of nano- $\text{VB}_2$  anode/air batteries, the effect of mechanical milling conditions on the discharge capacity of the obtained anodes were reported (Licht et al, 2012). It was indicated that sufficient thermal energy and impact conditions provided during ball milling process of V and B caused to impart the energy to  $\text{VB}_2$  from the elemental metals. Discharge efficiencies increased with increasing milling speed and decreased with over milling for 5 h. Anodes prepared in this study exhibited a volumetric and gravimetric capacity of  $20.7 \text{ kAh L}^{-1}$  and  $4.1 \text{ kAh kg}^{-1}$ , respectively. Thus, ball milling of V and B was a straightforward method to synthesize  $\text{VB}_2$  and to produce a material with very high discharge efficiency (Licht et al, 2012).

The effect of ball milling on the electrochemical performances of transition metal borides was also investigated in another study done by Wang et al (2012).  $\text{VB}_{0.5}$  was synthesized as aqueous anodes by mechanical milling of V and B and specific capacity of the obtained anodes was measured as  $2158 \text{ mAh g}^{-1}$  which is the highest value among the analysed metal borides.  $\text{VB}_{0.5}$  showed two discharge voltage

plateaus originated from electro-oxidation of vanadium and boride (Wang et al, 2012).

Figure 2.4 shows the energy capacity comparison of gasoline, hydrogen and electrochemical energy sources, adapted from the study of Licht et al (2008). As seen in Figure 2.4, VB<sub>2</sub> air cell energy capacity is several times higher than that of gasoline, hydrogen, conventional Zn anode and also all rechargeable batteries including Li ion, metal hydride or lead acid. Licht et al (2008) also considered a variety of borides including TaB, TaB<sub>2</sub>, MgB<sub>2</sub>, CrB<sub>2</sub>, CoB<sub>2</sub>, Ni<sub>2</sub>B and LaB<sub>6</sub> as alternative active anode materials. However, these borides did not exhibit significant discharge behaviour due to their high solubility in alkaline solution or their high reactivity with an alkaline electrolyte. Among the transition metal diborides, crystalline VB<sub>2</sub> showed the highest discharge capacity of >3300 mAh g<sup>-1</sup>. Thus, VB<sub>2</sub> has been strongly considered as an alternative active anode material for alkaline electrochemical storage cells (Licht et al, 2008). It has been further emphasized that the intrinsic anodic capacity of the VB<sub>2</sub> anode (20.7 kAh L<sup>-1</sup>) is tenfold higher than that of the lithium anode (2.06 kAh L<sup>-1</sup>) (Stuart et al, 2015).

A recent study described the discharge mechanism of the VB<sub>2</sub>/air cell by the overall cell reaction (2.1) (Stuart et al, 2015).



A net discharge process of VB<sub>2</sub>/air battery in the presence of a KOH electrolyte gave the products of K<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and KVO<sub>3</sub> (Stuart et al, 2015).

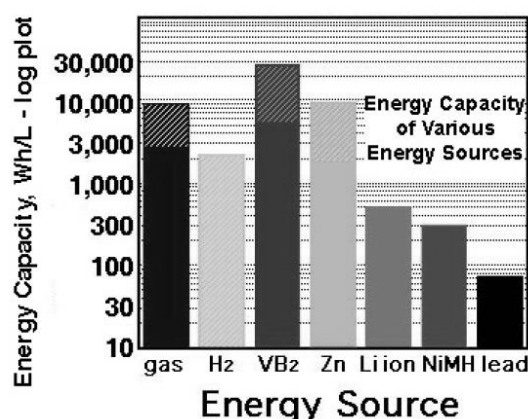
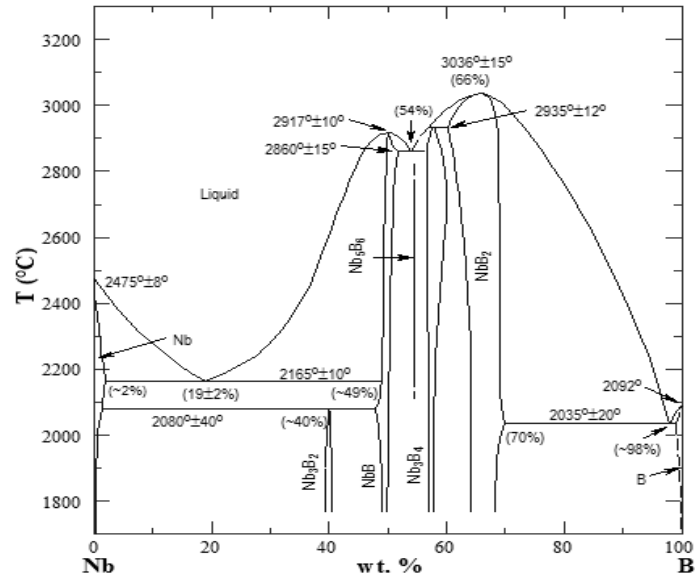


**Figure 2.4 :** Energy capacity comparison of gasoline, hydrogen and electrochemical energy sources, adapted from Licht et al (2008).

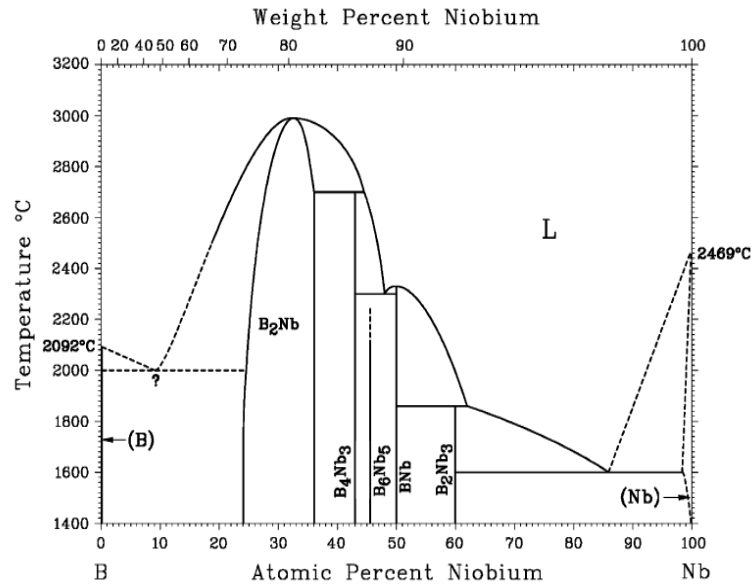
### 2.1.2 Properties and application areas of niobium borides

Niobium borides, like other borides of transition metals, are well known for their high melting point, high strength, high chemical stability and high thermal and electrical conductivity (Ivanovsky et al, 1998). Electronic properties of them result from the boron-boron interactions in boride structure whereas thermomechanical properties are due to the strength of the metal-metal, metal-boron and boron-boron bonds (Ivanovsky et al, 1998). It is further stated that chemical stability and cohesive properties of diborides is mainly controlled by the covalent boron-metal interaction and a comparison between diborides of IVA and VA group metals showed that  $\text{NbB}_2$  has the highest chemical stability (Ivanovsky et al, 1998). Furthermore,  $\text{NbB}_2$  is resistant to oxidizing acids but it is attacked by molten alkali (Aronsson, 1964).

Figure 2.5 shows the binary phase diagrams of Nb-B system proposed by Rudy and Windisch (1966) and Massalski (1990). Figure 2.5(b) shows the currently accepted Nb-B phase diagram and exhibits some differences with the diagram proposed by Rudy and Windisch (1966) (Figure 2.5(a)). The main differences are related to the stability of  $\text{Nb}_5\text{B}_6$  phase, the formation for the  $\text{Nb}_3\text{B}_2$  (peritectic or peritectoid), homogeneity range for  $\text{NbB}_2$  and the location of the B-rich eutectic point (Rudy and Windisch, 1966; Massalski, 1990). The Nb-B binary phase diagram given in Figure 2.5(b) illustrates four stable boride phases ( $\text{NbB}_2$ ,  $\text{Nb}_3\text{B}_4$ ,  $\text{NbB}$ ,  $\text{Nb}_3\text{B}_2$ ) and an unstable boride phase ( $\text{Nb}_5\text{B}_6$ ) (Massalski, 1990). It presents two congruently melting compounds  $\text{NbB}_2$  (at  $2980^\circ\text{C}$ ) and  $\text{NbB}$  (at  $2340^\circ\text{C}$ ), two incongruently melting compounds  $\text{Nb}_3\text{B}_4$  (at  $2700^\circ\text{C}$ ) and  $\text{Nb}_3\text{B}_2$  (at  $1860^\circ\text{C}$ ) and an unstable phase  $\text{Nb}_5\text{B}_6$  (at  $\sim 2240^\circ\text{C}$ ). According to the Nb-B phase diagram given in Figure 2.5(b),  $\text{NbB}_2$  is the most stable niobium boride phase and shows an extensive homogeneity range (25 – 35 at.% Nb) (Massalski, 1990).



(a)



(b)

**Figure 2.5 :** Binary phase diagrams of Nb-B system proposed by (a) Rudy and Windisch (1966) and (b) Massalski (1990).

The Nb-B phase diagram in Massalski (1990) was recently updated by Okamoto (2008) given in Figure 2.6. This diagram exhibits higher melting points of niobium boride phases than those of presented in the diagram given in Figure 2.5(b). NbB<sub>2</sub> phase has the highest melting point of 3020°C among niobium boride phases and shows a homogeneity range from 30 to 35 at.% Nb (Okamoto, 2008). In general, there is an agreement in the literature regarding the stability of the NbB, Nb<sub>3</sub>B<sub>4</sub> and NbB<sub>2</sub> phases, whereas the stability of Nb<sub>3</sub>B<sub>2</sub>, Nb<sub>5</sub>B<sub>6</sub> and Nb<sub>2</sub>B<sub>3</sub> phases is arguable (Junior et al, 2003).

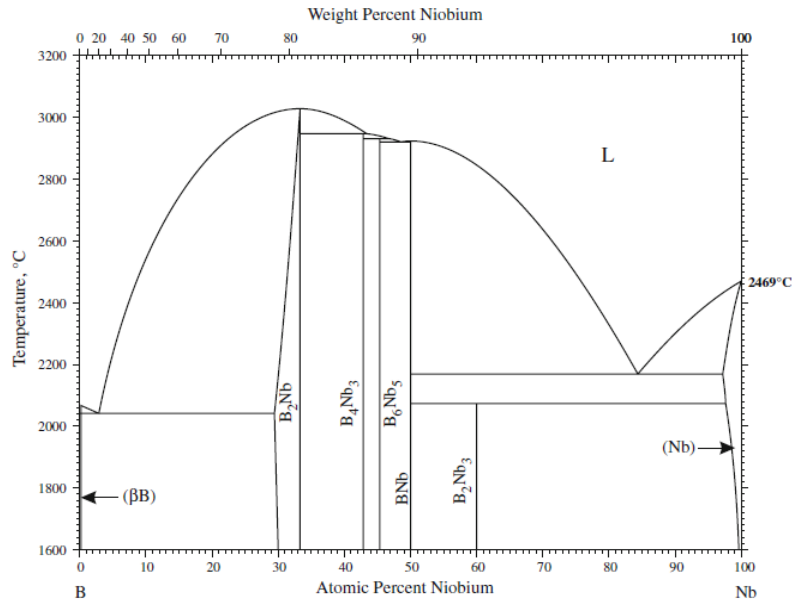


**Figure 2.6 :** Binary phase diagrams of Nb-B system proposed by Okamoto (2008).

The crystal structures of the phases  $\text{NbB}_2$ ,  $\text{Nb}_3\text{B}_4$ ,  $\text{Nb}_5\text{B}_6$ ,  $\text{NbB}$  and  $\text{Nb}_3\text{B}_2$  are of the  $\text{AlB}_2$ ,  $\text{Ta}_3\text{B}_4$ ,  $\text{V}_5\text{B}_6$ ,  $\text{CrB}$  and  $\text{U}_3\text{Si}_2$  types, respectively (Peçanha et al, 2007).  $\text{NbB}_2$  exhibits a hexagonal structure with a space group  $P6/mmm$ , in which Nb and B atoms occupy the 1a and 2d positions, respectively. The crystal structure of  $\text{NbB}_2$  is given in Figure 2.7 which is adapted from Hamdad et al (2010).  $\text{Nb}_3\text{B}_4$  has the orthorhombic structure with a space group  $Immm$ , in which Nb atoms occupy 2c and 4g positions and B atoms occupy 4g and 4h positions.  $\text{NbB}$  has the orthorhombic structure with a space group  $Cmcm$ , in which Nb and B atoms occupy 4c positions (Peçanha et al, 2007; Junior et al, 2003).

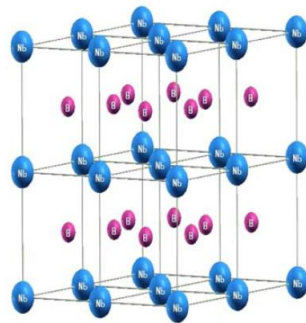


**Figure 2.7 :** The crystal structure of  $\text{NbB}_2$  adapted from Hamdad et al (2010).

Superconducting behaviour of niobium borides has been investigated in many reports for many years (Shein and Ivanovskii, 2002; Shein et al, 2003). The studies generally pointed out that stoichiometric niobium diboride did not have superconductivity

down to very low temperatures whereas non-stoichiometric niobium borides had superconductivity with different values of transition temperature. No clear superconductivity was observed down to 3 K in stoichiometric NbB<sub>2</sub> (Yamamoto et al, 2002). However, niobium-deficient NbB<sub>2</sub> prepared by sintering at 5 GPa gave superconductivity with superconducting critical temperature ( $T_c$ ) above 9 K. Nb<sub>0.76</sub>B<sub>2</sub> phase showed superconductivity with maximum value of 9.2 K (Yamamoto et al, 2002). Joseph et al (2003) studied the superconductivity in Nb<sub>1-x</sub>B<sub>2</sub> alloys and emphasized that  $T_c$  value is varied as a function of x. Takeya et al (2004) stated that Nb-deficient diborides in NbB<sub>2</sub> showed superconductivity with a transition up to 8 K. Mudgel et al (2008) also emphasized the non-superconductor behaviour of NbB<sub>2</sub> and proved the superconductivity in Nb-deficient niobium boride samples (NbB<sub>2+x</sub>) which showed diamagnetic signals in the temperature range of 8.9 – 11 K. Ren et al (2008) investigated the superconductivity for both of niobium-deficient and boron-deficient niobium boride phases and found that niobium and boron vacancies had different effects on the crystal lattice parameters and superconducting properties. Results showed that superconductivity only existed in niobium-deficient phases thanks to the niobium vacancies. On the other hand, it is claimed that boron vacancies cause to enhance the Nb-B bonding and break the superconductivity. The increase of B 2p<sub>π</sub> electronic states is crucial to the occurrence of superconductivity. A superconducting phase of Nb<sub>1.83</sub>B<sub>2</sub> was obtained with  $T_c$  of 9.3 – 9.9 K under optimum sintering conditions in temperatures between 700 and 1200°C (Ren et al, 2008).

Matsudaira et al (1989) measured a Vickers microhardness of 2600 kg/mm<sup>2</sup> of bulk NbB<sub>2</sub> (with a relative density of 98 %) prepared by sintering of Nb and B powders (at 1600°C for 15 min under 4 GPa). Otani et al (1998) observed similar Vickers hardness between the a- and c-planes of NbB<sub>2</sub> crystals (HV<sub>0.2</sub>=1950-2210 kg/mm<sup>2</sup>) prepared by the floating zone method and further stated that anisotropy is minimal. Furthermore, high temperature hardness of obtained NbB<sub>2</sub> crystals (1110-1130 kg/mm<sup>2</sup>) was considerably high as it compared to those of IVA group borides (Otani et al, 1998). Usta (2005) measured the Vickers microhardness of the niobium boride layer as HV = 2500 kg/mm<sup>2</sup> obtained by boronizing of pure niobium at 940°C for 8 h. Sairam et al (2014) reported the Vickers hardness of high density NbB<sub>2</sub> compacts (with a relative density of 97.7 %) as HV<sub>0.1</sub>=20.25 GPa prepared by spark

plasma sintering method (at 1900°C for 15 min under 70 MPa) from Nb and B powders. Furthermore, fracture toughness and elastic modulus of the high dense NbB<sub>2</sub> compact was measured as 4 MPa m<sup>1/2</sup> and 539 GPa, respectively (Sairam et al, 2014).

Table 2.2 summarizes the general properties of three niobium boride phases obtained from both experimental and theoretical studies. Increasing the boron content of the niobium boride phases leads to a decrease in the value of electrical resistivity. The same tendency is also exhibited by the coefficient of thermal expansion which is a maximum for NbB and a minimum for NbB<sub>2</sub> (Kovenskaya and Serebryakova, 1970). On the other hand, an increase was found in the work function, as the boron content of niobium boride phase increases (Samsonov et al, 1972). As shown in Table 2.2, niobium borides have high melting points (2340-3036°C) and high strengths (463-540 GPa).

**Table 2.2 :** General properties of niobium borides, adapted from Aronsson (1964), Rudy and Windisch (1966), Goldschmidt (1967), Kovenskaya and Serebryakova (1970), Samsonov et al (1972), Matsudaira et al (1989), Massalski (1990), Peçanha et al (2007), Miao et al (2011), Yao et al (2012), Qi et al (2014), Sairam et al (2014), Url-1.

| Properties                                           | NbB <sub>2</sub> | NbB          | Nb <sub>3</sub> B <sub>4</sub> |
|------------------------------------------------------|------------------|--------------|--------------------------------|
| Structure                                            | Hexagonal        | Orthorhombic | Orthorhombic                   |
| Theoretical density (g/cm <sup>3</sup> )             | 6.87             | 7.56         | 6.96                           |
| Melting point (°C)                                   | 2980-3036        | 2340-2900    | 2700-2900                      |
| Electrical resistivity (μΩ.cm)                       | 25.7             | 40-64        | 33.5                           |
| Thermal conductivity (W/cm.K)                        | 0.24             | -            | -                              |
| Thermal expansion coefficient (10 <sup>-6</sup> /°C) | 7.7              | 12.9         | 9.9                            |
| Work function (eV)                                   | 4                | 3.6          | 3.9                            |
| Hardness (GPa)                                       | 18-28.3          | 27.1         | 23-31.3                        |
| Young's modulus (GPa)                                | 478-540          | 463          | 497-505                        |

Due to their attractive combination of properties, niobium borides have received a great deal of attention owing to their applications in mechanical industry, chemistry and microelectronics fields (Torabi et al, 2015). Especially the compound, NbB<sub>2</sub>, is recognized as the potential candidate for high temperature structural applications (Ma et al, 2009). NbB<sub>2</sub> is known as a refractory and a coating material which has excellent oxidation stability at high temperatures (Motojima et al, 1975). It has been also reported that niobium borides are suitable as coatings for high-current hot cathodes due to their resistant to high temperatures and low work functions (Url-2).

NbB<sub>2</sub> has been reported as an electrode for use in the refining of aluminium (Murata, 1971). This patent claimed that sintered body of niobium boride had higher corrosion resistance in molten aluminium and longer useful life as an electrode than the bodies of zirconium, titanium and tantalum borides (Murata, 1971). Besides, another patent suggested niobium boride as current-conducting element in contact with molten aluminium in electrolytic cells (Morgan, 1963). As mentioned before, non-stoichiometric compounds of niobium diboride have been a matter in many reports as potential superconductors (Shein and Ivanovskii, 2002; Yamamoto et al, 2002; Joseph et al, 2003; Ren et al, 2008; Mudgel et al, 2008). Nb-deficient diborides in NbB<sub>2</sub> showed superconductivity with a transition up to 11 K which makes to use it as superconducting materials (Mudgel et al, 2008).

## 2.2 Production and Sintering Techniques

Many production techniques have been applied in the preparation of vanadium and niobium borides. Table 2.3 is the summary of the production techniques of vanadium and niobium borides. Various stoichiometries of these borides have been fabricated conventionally by high temperature methods such as borothermal/carbothermal reduction processes of metal oxides and B<sub>2</sub>O<sub>3</sub> or B, direct solid-phase reactions or arc melting using corresponding elemental metals and B (Peshev et al, 1968; Peshev et al, 1968; Matsumoto et al, 1982; Jha et al, 2011; Yu and Lundström, 1995; Bulfon et al, 1997; Nunes et al, 2004; Junior et al, 2003; Takahashi et al, 2005; Nunes et al, 2005; Makarenko et al, 1998; Maeda et al, 1994; Okada et al, 2008; Matsudaira et al, 1989; Cheng et al, 2013). Another traditional technique to synthesize diborides of niobium is chemical vapour deposition using gas mixtures of NbCl<sub>5</sub>, BCl<sub>3</sub> and H<sub>2</sub> (Motojima et al, 1975). In order to obtain single crystals of vanadium and niobium diborides, floating zone method has been also applied using VB<sub>2</sub> and NbB<sub>2</sub> starting materials (Nakano et al, 1981; Otani et al, 1998). The recent techniques developed for preparing vanadium and niobium borides are self-propagating high-temperature synthesis (SHS) (Yeh and Wang, 2011; Takeya et al, 2004; Tsuchida and Kakuta, 2005; Yeh and Chen, 2006a; Yeh and Chen, 2006b; Tsuchida and Kakuta, 2007; Yeh and Wang, 2010), low-temperature synthesis in an autoclave (Shi et al, 2004; Cai et al, 2005; Ma et al, 2009) and ball milling and mechanochemical synthesis (Kim et al, 2008; Wang et al, 2010; Licht et al, 2012; Morris and Morris, 1991; Iizumi et al, 2006; Torabi et al, 2015; Jafari et al, 2015). SHS processes were conducted using

V/B, Nb/B and Nb<sub>2</sub>O<sub>5</sub>/B powder mixtures to achieve vanadium and niobium borides with various stoichiometries (Yeh and Wang, 2011; Takeya et al, 2004; Yeh and Chen, 2006a; Yeh and Chen, 2006b; Yeh and Wang, 2010). Besides, utilization of Nb/B/C starting materials resulted in the formation of NbB<sub>2</sub>-NbC composite powders (Tsuchida and Kakuta, 2005; Tsuchida and Kakuta, 2007). On the other hand, low-temperature synthesis of VB<sub>2</sub> and NbB<sub>2</sub> nanocrystallites and nanorods were carried out using an autoclave from the reactants of corresponding metal chlorides/NaBH<sub>4</sub>/Mg and Nb<sub>2</sub>O<sub>5</sub>/B<sub>2</sub>O<sub>3</sub>/Mg in the presence of NaCl/MgCl<sub>2</sub> solvent (Shi et al, 2004; Cai et al, 2005; Ma et al, 2009). Ball milling of V/B and Nb/B were applied to obtain VB<sub>x</sub>-V alloys, VB<sub>2</sub> nanopowders, NbB and NbB<sub>2</sub> (Wang et al, 2010; Licht et al, 2012; Morris and Morris, 1991; Iizumi et al, 2006). Mechanochemical synthesis of the VCl<sub>3</sub>/LiBH<sub>4</sub>/LiH and Al/Mg/B<sub>2</sub>O<sub>3</sub>/Nb reactants gave the final products of VB<sub>2</sub> and NbB<sub>2</sub> nanopowders (Kim et al, 2008; Jafari et al, 2015). Besides, NbB<sub>2</sub>-NbC composite powders were achieved by mechanochemical reaction of Mg/B<sub>2</sub>O<sub>3</sub>/Nb/C reactants (Torabi et al, 2015).

The application of high temperatures, the use of expensive starting materials (elemental V/Nb or B) and/or the use of complicated equipment may restrict the fabrication process to obtain vanadium and niobium borides for the demanded applications. Conventional techniques have some general restrictions such as high temperature operation, the formation of by-products and non-uniform phases and grain growth during processing. Thus, it is necessary to find an effective technique that could overcome these limitations and represent the advantages of time and energy savings, simplicity and high-purity products. Furthermore, considering the control over the microstructure (shape, size etc.) and the refinement of the resultant products is essential for many application areas.

**Table 2.3 :** Summary of the production techniques of vanadium and niobium borides.

| Production Techniques                                                                                                               | Reactants                                                                                   | Final Products                                                                                                           | References                |
|-------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------|---------------------------|
| High Temperature Methods                                                                                                            |                                                                                             |                                                                                                                          |                           |
| - Borothermal reaction<br><br>- Arc melting<br><br><br><br><br><br><br><br>- Carbothermal reaction<br>- Direct solid-state reaction | V <sub>2</sub> O <sub>3</sub> , B                                                           | VB <sub>2</sub> -VB                                                                                                      | Peshev et al, 1968        |
|                                                                                                                                     | Nb <sub>2</sub> O <sub>5</sub> , B                                                          | NbB <sub>2</sub>                                                                                                         | Peshev et al, 1968        |
|                                                                                                                                     | Nb <sub>2</sub> O <sub>5</sub> , B                                                          | NbB <sub>2</sub>                                                                                                         | Matsumoto et al, 1982     |
|                                                                                                                                     | NbO <sub>2</sub> , B                                                                        | NbB <sub>2</sub>                                                                                                         | Jha et al, 2011           |
|                                                                                                                                     | V/Nb, B                                                                                     | (V <sub>1-x</sub> Nb <sub>x</sub> ) <sub>2</sub> B <sub>3</sub>                                                          | Yu and Lundström, 1995    |
|                                                                                                                                     | V, B                                                                                        | VB <sub>2</sub> single crystals                                                                                          | Bulfon et al, 1997        |
|                                                                                                                                     | V, B                                                                                        | V <sub>3</sub> B <sub>4</sub> -V <sub>5</sub> B <sub>6</sub> -VB                                                         | Nunes et al, 2004         |
|                                                                                                                                     | Nb, B                                                                                       | Nb <sub>3</sub> B <sub>2</sub> -Nb-NbB                                                                                   | Junior et al, 2003        |
|                                                                                                                                     | Nb, B                                                                                       | NbB <sub>2</sub>                                                                                                         | Takahashi et al, 2005     |
|                                                                                                                                     | Nb, B                                                                                       | NbB <sub>x</sub>                                                                                                         | Nunes et al, 2005         |
|                                                                                                                                     | Metal oxides, B <sub>4</sub> C                                                              | VB <sub>2</sub> -B <sub>4</sub> C                                                                                        | Makarenko et al, 1998     |
|                                                                                                                                     | Nb <sub>2</sub> O <sub>5</sub> , B <sub>2</sub> O <sub>3</sub> , C                          | NbB <sub>2</sub> -NbC                                                                                                    | Maeda et al, 1994         |
|                                                                                                                                     | V, B                                                                                        | V <sub>3</sub> B <sub>4</sub> -V <sub>2</sub> B <sub>3</sub> -VB <sub>2</sub>                                            | Okada et al, 2008         |
|                                                                                                                                     | Nb, B                                                                                       | NbB <sub>2</sub> , NbB, Nb <sub>3</sub> B <sub>4</sub> single phases                                                     | Matsudaira et al, 1989    |
|                                                                                                                                     | Nb, B                                                                                       | NbB <sub>x</sub>                                                                                                         | Cheng et al, 2013         |
| Chemical Vapour Deposition (CVD)                                                                                                    | NbCl <sub>5</sub> , BCl <sub>3</sub> , H <sub>2</sub>                                       | NbB <sub>2</sub>                                                                                                         | Motojima et al, 1975      |
| Floating zone method                                                                                                                | VB <sub>2</sub>                                                                             | VB <sub>2</sub> single crystal                                                                                           | Nakano et al, 1981        |
|                                                                                                                                     | NbB <sub>2</sub>                                                                            | NbB <sub>2</sub> single crystal                                                                                          | Nakano et al, 1981        |
|                                                                                                                                     | NbB <sub>2</sub> , B                                                                        | NbB <sub>2</sub> single crystals                                                                                         | Otani et al, 1998         |
| Self-propagating high-temperature synthesis (SHS)                                                                                   | V, B                                                                                        | VB single phase, VB-V <sub>3</sub> B <sub>4</sub> and VB <sub>2</sub> -V <sub>3</sub> B <sub>4</sub> -VB                 | Yeh and Wang, 2011        |
|                                                                                                                                     | Nb, B                                                                                       | Nb <sub>x</sub> B <sub>2</sub> (x=0.67-1.11)                                                                             | Takeya et al, 2004        |
|                                                                                                                                     | Nb, B, C                                                                                    | NbB <sub>2</sub> -NbC                                                                                                    | Tsuchida and Kakuta, 2005 |
|                                                                                                                                     | Nb, B                                                                                       | Nb <sub>3</sub> B <sub>2</sub> , NbB, Nb <sub>5</sub> B <sub>6</sub> , Nb <sub>3</sub> B <sub>4</sub> , NbB <sub>2</sub> | Yeh and Chen, 2006a       |
|                                                                                                                                     | Nb, B                                                                                       | NbB, NbB <sub>2</sub>                                                                                                    | Yeh and Chen, 2006b       |
|                                                                                                                                     | Nb, B, C                                                                                    | NbB <sub>2</sub> -NbC                                                                                                    | Tsuchida and Kakuta, 2007 |
|                                                                                                                                     | Nb <sub>2</sub> O <sub>5</sub> , B                                                          | NbB <sub>2</sub>                                                                                                         | Yeh and Wang, 2010        |
| Low temperature synthesis in an autoclave                                                                                           | VCl <sub>4</sub> , NaBH <sub>4</sub> , Mg                                                   | VB <sub>2</sub> nanocrystallites                                                                                         | Shi et al, 2004           |
|                                                                                                                                     | NbCl <sub>5</sub> , NaBH <sub>4</sub>                                                       | NbB <sub>2</sub> nanorods                                                                                                | Cai et al, 2005           |
|                                                                                                                                     | Nb <sub>2</sub> O <sub>5</sub> , B <sub>2</sub> O <sub>3</sub> , Mg, NaCl-MgCl <sub>2</sub> | NbB <sub>2</sub> nanocrystallites                                                                                        | Ma et al, 2009            |
| Ball milling and mechanochemical synthesis                                                                                          | VCl <sub>3</sub> , LiBH <sub>4</sub> , LiH                                                  | VB <sub>2</sub> nanopowders                                                                                              | Kim et al, 2008           |
|                                                                                                                                     | V, B                                                                                        | VB <sub>x</sub> -V alloys                                                                                                | Wang et al, 2010          |
|                                                                                                                                     | V, B                                                                                        | VB <sub>2</sub> nanopowders                                                                                              | Licht et al, 2012         |
|                                                                                                                                     | Nb, B                                                                                       | NbB, NbB <sub>2</sub>                                                                                                    | Morris and Morris, 1991   |
|                                                                                                                                     | Nb, B                                                                                       | NbB <sub>2</sub>                                                                                                         | Iizumi et al, 2006        |
|                                                                                                                                     | Mg, B <sub>2</sub> O <sub>3</sub> , Nb, C                                                   | NbC-NbB <sub>2</sub>                                                                                                     | Torabi et al, 2015        |
|                                                                                                                                     | Al/Mg, B <sub>2</sub> O <sub>3</sub> , Nb                                                   | NbB <sub>2</sub> nanocrystallites                                                                                        | Jafari et al, 2015        |

Few studies exist in the literature relating the consolidation of vanadium and niobium borides. Recent studies are mainly focused on the sintering of niobium borides using various techniques including high pressure sintering and spark plasma sintering (SPS) of elemental Nb and B powder mixtures (Matsudaira et al, 1989; Yamamoto et al, 2002; Sairam et al, 2014) and pressureless sintering using NbB<sub>2</sub>/B/Nb starting materials (Mudgel et al, 2008; Ren et al, 2008). Table 2.4 is the summary of the sintering techniques of the niobium borides. Sintering studies have been mostly carried out in order to investigate superconducting behaviour of niobium borides (Yamamoto et al, 2002; Mudgel et al, 2008; Ren et al, 2008). Only the studies conducted by Matsudaira et al (1989) and Sairam et al (2014) reported the mechanical properties (i.e. microhardness, fracture toughness, elastic modulus) of the sintered niobium boride bodies.

**Table 2.4 :** Summary of the sintering techniques of the niobium borides.

| <b>Sintering Techniques</b>  | <b>Starting Materials</b> | <b>Sintering Conditions</b>                                                                    | <b>References</b>      |
|------------------------------|---------------------------|------------------------------------------------------------------------------------------------|------------------------|
| High-pressure sintering      | Nb, B                     | Preheated at 1000°C for 60 min and sintered at 1600°C under 4 GPa                              | Matsudaira et al, 1989 |
| High-pressure sintering      | Nb, B                     | Preheated at 900-1300°C for 10 min and sintered in a BN tube under 1-5 GPa for 0.5-2 h         | Yamamoto et al, 2002   |
| Pressureless sintering       | NbB <sub>2</sub> , B      | Palletized and encapsulated in iron tubes and sintered in a tubular furnace at 1100°C for 20 h | Mudgel et al, 2008     |
| Pressureless sintering       | NbB <sub>2</sub> , B/Nb   | Pressed into pellets and sintered in an electrical muffle furnace at 600-1500°C for 72 h       | Ren et al, 2008        |
| Spark Plasma Sintering (SPS) | Nb, B                     | Spark plasma sintered at 1700-1900°C under 30-70 MPa                                           | Sairam et al, 2014     |

### 2.2.1 Production techniques of vanadium borides

Traditional techniques for producing vanadium borides have been mainly focused on the high temperature methods such as borothermal and carbothermal reductions of vanadium oxides (Peshev et al, 1968; Makarenko et al, 1998) and arc melting or direct solid state reactions of V and B (Yu and Lundström, 1995; Bulfon et al, 1997; Nunes et al, 2004; Okada et al, 2008).

Peshev et al (1968) reported the borothermal preparation of vanadium borides using the reaction of V<sub>2</sub>O<sub>3</sub> with B. Stoichiometric mixtures of V<sub>2</sub>O<sub>3</sub> and B were prepared

according to the reaction (2.2), pressed into pellets and heat-treated within the temperature range of 1000-1750°C under vacuum.



Vanadium borides including the mixtures of  $\text{VB}_2$  and VB phases were obtained after heating at 1700-1750°C, without any vanadium oxide impurity. The reason of the simultaneous formation of  $\text{VB}_2$  and VB phases was explained by considering the dependence of  $\Delta G^\circ_{\text{T}}$  on temperature for the reactions (2.2) and (2.3).

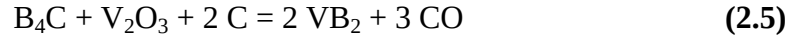
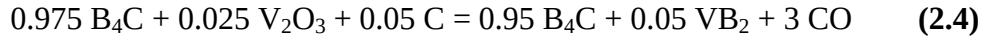


$\text{VB}_2$  could not be obtained as a single-phase because the simultaneous formation of  $\text{VB}_2$  and VB phases was thermodynamically feasible especially at temperatures above 1700°C, at which both the reactions (2.2) and (2.3) had the negative values (Peshev et al, 1968).

Yu and Lundström (1995) reported the synthesis of  $(\text{V}_{1-x}\text{Nb}_x)_2\text{B}_3$  ternary borides by arc melting of B, V and Nb starting materials followed by heat treatment. In order to prepare polycrystalline samples of  $(\text{V}_{1-x}\text{Nb}_x)_2\text{B}_3$ , the mixtures of the starting materials were pressed into pellets, arc-melted under Ar atmosphere and subsequently heat treated in a resistance furnace at 1300°C for 24 h under Ar atmosphere. In order to prepare single crystals of  $(\text{V}_{1-x}\text{Nb}_x)_2\text{B}_3$ , the mixtures of the B, V, Nb and Al starting materials placed in an alumina crucible were heated treated in a graphite furnace at 1650°C for 5 h and then cooled to 1000°C with a cooling rate of 50°C/h and then the furnace was switched off. As-grown crystals were leached in 6 M HCl to remove the solidified excess aluminium. It was indicated that the initial V/Nb ratio affected the unit cell parameters of the ternary boride (Yu and Lundström, 1995).

Bulfon et al (1997) reported the synthesis of  $\text{VB}_2$  single crystal by arc melting of V ingots and B powders which was compacted into pellets. Microhardness measurements of the single crystals were carried out as a function of crystallographic orientation. The microhardness value of the single crystal was measured as  $\text{HV}_{0.02} = 30.6 \text{ GPa}$  in the  $\{10.0\}$  direction that shows slightly higher values than the other directions like  $\{00.1\}$  and  $\{10.1\}$ . It was claimed that this is due to the strong B-B bonds in the basal plane of the  $\text{AlB}_2$  structure (Bulfon et al, 1997).

Makarenko et al (1998) studied the carbothermal production of VB<sub>2</sub>-B<sub>4</sub>C composites by using B<sub>4</sub>C-V<sub>2</sub>O<sub>3</sub>-C and B<sub>2</sub>C-V<sub>2</sub>O<sub>3</sub> systems in a vacuum furnace at the temperature ranges of 1200-1800 K for 1 h. Experimental studies were carried out in regard of the reactions (2.4) and (2.5) and also the components of B<sub>2</sub>C + V<sub>2</sub>O<sub>3</sub> in equimolar ratio.



VB<sub>2</sub> and B<sub>4</sub>C phases without any oxide or intermediate phases could be obtained in vacuum at 1800 K in case of using reaction (2.4). Addition of free C (reaction (2.5)) decreased the formation temperature of the boride phase and led to the appearance of VC phase at the same temperatures (Makarenko et al, 1998).

Nunes et al (2004) investigated the stability of V<sub>5</sub>B<sub>6</sub> phase by using the methods of arc melting of V and B and their subsequent heat treatment under high-vacuum at 2000°C for 2 h. The nominal alloy compositions of V48B52, V45.45B54.55 and V44B56 were prepared between the VB phase (50 at. % B) and V<sub>3</sub>B<sub>4</sub> phase (57.14 at. % B) with respect to the V-B phase diagram given in Figure 2.1(b). XRD patterns of V48B52 alloy in both as-cast and heat-treated conditions gave the reflections of V<sub>5</sub>B<sub>6</sub> and VB phases. Although V<sub>3</sub>B<sub>4</sub> was expected as primary phase during solidification of this alloy according to the V-B phase diagram (Figure 2.1), there was no indication of V<sub>3</sub>B<sub>4</sub>. On the other hand, the other two alloys (V45.45B54.55 and V44B56) contained V<sub>3</sub>B<sub>4</sub>, V<sub>5</sub>B<sub>6</sub> and VB phases in their as-cast and heat-treated microstructures. The presence of same phases observed in both as-cast and heat-treated samples indicated that equilibrium conditions could not be achieved even after heating at 2000°C for 2 h. It was concluded that V<sub>5</sub>B<sub>6</sub> formed through the  $\text{L} + \text{V}_3\text{B}_4 \leftrightarrow \text{V}_5\text{B}_6$  peritectic reaction and it should be stable at 2000°C, in disagreement with currently accepted V-B phase diagram (Nunes et al, 2004).

Okada et al (2008) reported the preparation of V<sub>2</sub>B<sub>3</sub> single crystals by the high temperature Al-solution method using V chips and crystalline B powders as starting materials. The mixtures of V metal chips, crystalline B powders and Al metal chips in atomic ratios of B/V=1.4-1.7 and Al/V=0.9-47.2 were placed in an alumina crucible, heat treated in a furnace under Ar atmosphere at the temperature range of 1400-1700°C for 5 h and cooled slowly to 1000°C at the rate of 50°C/h. The as-grown crystals were separated from the solidified matrix by dissolving the excess Al

in HCl. Results showed that only the three borides  $V_3B_4$ ,  $V_2B_3$  and  $VB_2$  were formed within the B/V ratio range of 1.4-1.7. It is stated that the more boron-rich phases formed for the larger B/V values in the starting materials. The phase composition of vanadium borides affected by varying the reaction temperature and composition of the starting materials and mixtures of vanadium boride phases in different stoichiometries were obtained.  $V_2B_3$  crystals as the dominant phase were obtained at 1500 to 1700°C together with  $V_3B_4$  and  $VB_2$  crystals. The optimum conditions for obtained relatively large crystals of  $V_2B_3$  were found to include atomic ratios of starting materials B/V=1.45 and Al/V=28.32 at 1600°C for 5 h (Okada et al, 2008).

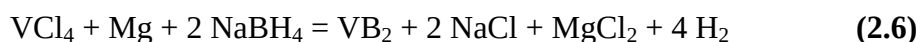
In order to obtain  $VB_2$  single crystals, floating zone method has been also applied (Nakano et al, 1981). Nakano et al (1981) reported single crystal growth of  $VB_2$  by a radio frequency floating zone method using  $VB_2$  powders with a purity of 99 %. Feed rods were made by sintering at 1900°C and crystal growth was carried out in a high frequency heating system under Ar atmosphere. Single phase  $VB_2$  products containing single crystals of 3-5 mm in diameter were obtained with total metallic impurities less than 0.9 wt. % (Nakano et al, 1981).

Even though many transition metal borides have been fabricated by combustion synthesis, few studies have been performed on the preparation of vanadium borides by self-propagating high-temperature synthesis (SHS) (Yeh and Wang, 2011). A study done by Yeh and Wang (2011) represented the first attempt to investigate the feasibility of fabricating various vanadium borides ( $V_3B_2$ , VB,  $V_5B_6$ ,  $V_3B_4$ ,  $V_2B_3$  and  $VB_2$ ) by combustion synthesis from elemental V and B powder compacts of their corresponding stoichiometries. The reactant powders with different molar ratios including V:B=3:2, 1:1, 5:6, 3:4, 2:3 and 1:2 were mixed in a ball mill at 120 rpm for 10 h and milled powders were cold pressed into cylindrical compacts. SHS experiments were conducted in a stainless-steel combustion chamber under Ar atmosphere. Single phase VB was achieved using the powder compacts of V:B=1:1, 5:6 and 3:4. The resulting product of the sample with V:B=3:2 also contained VB, however, with a large amount of unreacted V, implying an incomplete phase conversion. Final product obtained from the powder compacts of V:B=2:3 contained two boride phases VB and  $V_3B_4$ . For the powder compacts of V:B=1:2,  $VB_2$  was formed as the dominant phase with VB and  $V_3B_4$  as the trivial phases. It was concluded that among six vanadium borides, VB and  $VB_2$  were the only two borides

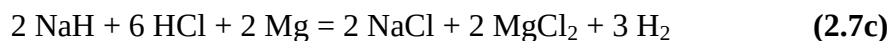
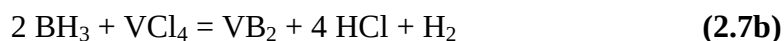
produced almost monolithically from the powder compacts of their corresponding stoichiometries. However, some vanadium boride phases, like  $V_3B_2$ ,  $V_5B_6$  and  $V_2B_3$ , could not be observed in any resultant products suggesting that the formation of them were kinetically unfavourable by combustion of their constituent elements. It was also claimed that the reason of the absence of these borides was due to their crystal structures which were too complicated to form during combustion process subjected to a fast cooling rate (Yeh and Wang, 2011).

$VB_2$  nanopowders have been prepared by low temperature synthesis and mechanochemical synthesis methods using vanadium chloride as starting material (Shi et al, 2004; Kim et al, 2008). Furthermore, some studies have been carried out to investigate the electrochemical performances of  $VB_x$ -V alloys and  $VB_2$  nanopowders which have been obtained by ball milling of V and B (Wang et al, 2010; Licht et al, 2012).

A new simple synthesis route to prepare vanadium boride was developed by Shi et al (2004). Shi et al (2004) reported the low temperature synthesis of nanocrystalline  $VB_2$  in an autoclave at  $650^\circ\text{C}$  for 8 h using the powder mixtures of  $VCl_4$ ,  $NaBH_4$  and Mg in regard of the overall reaction (2.6).



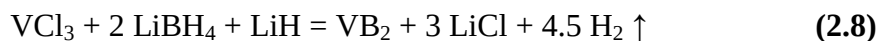
After the reaction in autoclave,  $NaCl$ ,  $MgCl_2$  and other impurities were removed by leaching respectively with absolute ethanol, dilute  $HCl$  and distilled water. The final powders were obtained after drying in vacuum at  $60^\circ\text{C}$  for 4 h. The reaction mechanism in autoclave was explained in regard of the reactions (2.7a) through (2.7c).



$NaBH_4$  decomposed to generate gaseous  $BH_3$  and  $NaH$ , with the temperature increasing up to  $400^\circ\text{C}$  in autoclave and at  $650^\circ\text{C}$  gaseous  $VCl_4$  and  $BH_3$  reacted to produce  $VB_2$ . Then, the produced  $HCl$  reacted with  $NaH$  and  $Mg$  powders to form  $NaCl$ ,  $MgCl_2$  and  $H_2$ . It was emphasized that the high pressure in the autoclave, coming from the produced  $H_2$  gas made the crystalline  $VB_2$  form at a relatively low

temperature (650°C). Single phase VB<sub>2</sub> crystallites were composed of uniform particles with the grain size in the range of 50 – 100 nm (Shi et al, 2004).

VB<sub>2</sub> nanopowders were synthesized by mechanochemical reaction using the raw materials of VCl<sub>3</sub>, LiBH<sub>4</sub> and LiH in regard of the reaction (2.8) (Kim et al, 2008).



LiCl as a process control agent was also added to the mixtures in order to prevent the increase in temperature during milling and hence the particle growth of the reaction products. Mixtures were milled up to 4 h in a planetary ball mill with a rotation speed of 500 rpm using a BPR of 30:1. Milled powders were then leached in distilled water, ethanol and acetone in order to remove LiCl produced as a by-product according to the reaction (2.8). After milling and leaching experiments, VB<sub>2</sub> nano powders were obtained with particle sizes in the range between 15 and 60 nm (Kim et al, 2008). Additionally, there is a patent application of the same research group relating to the preparation of the transition metal borides including vanadium and niobium borides (Shim et al, 2008). The production method of this invention included the similar processes applied in the study done by Kim et al (2008) (Shim et al, 2008).

A series of VB<sub>x</sub> (x=0.1, 0.25, 0.5 and 1) were prepared by high energy ball milling using the mixtures of elemental V and B powders with different atomic ratios and tested as alternative high capacity anodic materials for air batteries (Wang et al, 2010). Milling was performed at 1200 rpm for 10 h with a BPR of 12:1. Results showed that all the resultant products contained elemental V due to the insufficient amount of B that could not ensure the complete transformation of V into vanadium borides. The amount of the remained V decreased with increasing B content and became indistinct at V:B=1. However, the XRD patterns of the sample with V:B=1 showed featureless bands at 2θ=35-45°, suggesting the formation of amorphous alloys of B and V during milling (Wang et al, 2010).

Licht et al (2012) investigated the nano-VB<sub>2</sub> synthesis by mechanical alloying of V and B powders in the ratio of 2:1 and optimized the production parameters of VB<sub>2</sub> for use as a high capacity anode material with enhanced charge transfer and increase voltage. Milling experiments were performed by using a planetary ball mill for 10 and 20 min, 3, 4 and 5 h with milling speeds of 200, 400, 500 and 600 rpm. After

only milling for 20 min at 600 rpm, vanadium-boron mix consisted of a heterogeneous distribution of the particles in the range between 100 and 400 nm. Resultant powders obtained by milling for 4 h at 600 rpm contained the VB<sub>2</sub> phase with the presence of unreacted V (Licht et al, 2012).

### 2.2.2 Production techniques of niobium borides

Traditional techniques for producing niobium borides have been mainly focused on the high temperature methods such as borothermal and carbothermal reductions of niobium oxides (Peshev et al, 1968; Matsumoto et al, 1982; Maeda et al, 1994; Jha et al, 2011) and arc melting or direct solid-state reactions of Nb and B (Matsudaira et al, 1989; Junior et al, 2003; Takahashi et al, 2005; Nunes et al, 2005; Cheng et al, 2013).

Peshev et al (1968) reported the borothermal preparation of niobium borides using the reaction of Nb<sub>2</sub>O<sub>5</sub> with B. Stoichiometric mixtures of Nb<sub>2</sub>O<sub>5</sub> and B were prepared according to the reaction (2.9), pressed into pellets and heat-treated within the temperature range of 1000-1750°C under vacuum.



Niobium borides with a composition close to that of stoichiometric NbB<sub>2</sub> was obtained after heating at 1650°C for 1 h (Peshev et al, 1968).

NbB<sub>2</sub> was prepared from the mixture of Nb<sub>2</sub>O<sub>5</sub> and B which is heated to 3000°C and annealed at 2000°C in Ar plasma arc, according to the reaction (2.9) (Matsumoto et al, 1982). Niobium borides were synthesized by solid state reaction between Nb and B at different temperatures (Matsudaira et al, 1989). Single phases of NbB and NbB<sub>2</sub> were obtained by heating at 1000°C for 60 min using the mixtures with respective stoichiometries. A single phase of Nb<sub>3</sub>B<sub>4</sub> was obtained at higher temperature of 1800°C (Matsudaira et al, 1989).

Junior et al (2003) investigated the new data on phase equilibrium of the Nb-B system by arc melting of Nb and B under pure Ar and subsequent heat treatment at 1700°C for 16 h. As-cast Nb-B alloys with compositions of 16 at. % B and 40 at. % B consisted of Nb<sub>ss</sub> (solid solution) (with a small amount of NbB) and NbB (with a small amount of Nb<sub>ss</sub>), respectively. After heat treatment at 1700°C for 16 h, XRD pattern of the Nb-B alloys with composition of 16 at. % B gave only the peaks of

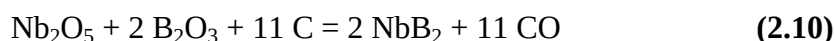
Nb<sub>ss</sub> and Nb<sub>3</sub>B<sub>2</sub>, indicating the dissolution of initially present NbB phase. On the other hand, after heat treatment, XRD pattern of the Nb-B alloys with composition of 40 at. % B presented the peaks of Nb<sub>3</sub>B<sub>2</sub>, in addition to those of Nb<sub>ss</sub> and NbB. Moreover, during heat treatment of the alloys at 1700°C, no liquid formation was observed (Junior et al, 2003).

NbB<sub>2</sub> was prepared by melting of 1:3 nominal mixtures of the Nb and B chunks using a tri-arc furnace and its superconductivity was investigated (Takahashi et al, 2005). Samples gave two-step superconducting transition as a function of temperature which was originated from the two different phases with compositional ratios of Nb:B=1:2.9 and 1:12 (Takahashi et al, 2005). Another study on the preparation of niobium borides using arc melting and investigation of their superconducting behaviour reported that Nb-deficient samples were found to contain traces of superconducting phase with T<sub>c</sub> ≈ 3.5 K (Nunes et al, 2005).

Jha et al (2011) suggested a novel borothermal route at 1300°C for the synthesis of nanocrystalline niobium oxide and niobium diboride using an amorphous niobium precursor. Niobium precursor was mixed with boron in the ratio of 1:12 and annealed at 1300°C for 150 min under an Ar atmosphere to yield NbO<sub>2</sub>. Then, NbO<sub>2</sub> was mixed with boron in the ratio of 1:6 and annealed at 1300°C for 150 min under an Ar atmosphere to yield NbB<sub>2</sub> (Jha et al, 2011).

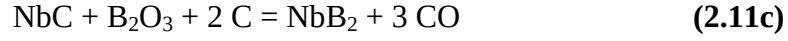
Synthesis of niobium boride nanoparticle by RF thermal plasma was studied using the feeding powders of Nb and crystalline B with feed rates of 0.2, 0.5 and 1.0 g/min under atmospheric pressure (Cheng et al, 2013). The mass fraction of niobium boride in the final product decreased and the crystalline size of niobium boride nanoparticles increased with increasing powder feed rate (Cheng et al, 2013).

Carbothermal production of NbB<sub>2</sub> (with a residual carbon content of 2.65 % by mass) was achieved in a vertical tubular reactor at 1800°C using the powder mixtures of Nb<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub> and C according to the reaction (2.10) (Maeda et al, 1994).



It is stated that carbothermal reduction process has advantages such as diminishing grain growth due to particle agglomeration, providing the formation of microcrystalline powder and escaping the gaseous by-products. The mechanism of

the carbothermal reaction process was described by the following reactions (2.11a), (2.11b) and (2.11c).



Moreover, it is emphasized that the initial size of precursor particles and reaction temperature had a significant role on the formation yield and microstructure of NbB<sub>2</sub>. NbB<sub>2</sub> and NbC phases with small amounts of B<sub>2</sub>O<sub>3</sub> and NbO<sub>2</sub> were obtained when the size of precursor particles were 60 μm after the carbothermal reduction at 1650°C. If the size of precursor particles decreased to 5 μm, Nb<sub>2</sub>O<sub>5</sub> was converted nearly completely to NbB<sub>2</sub> after the reaction. Furthermore, as the reaction temperature increased from 1600 to 1800°C, the amount of NbC phase decreased and the crystallite size of NbB<sub>2</sub> increased from 40-50 nm to 200-300 nm (Maeda et al, 1994).

Another traditional technique to synthesize diborides of niobium is chemical vapour deposition using gas mixtures of NbCl<sub>5</sub>, BCl<sub>3</sub> and H<sub>2</sub> (Motojima et al, 1975).

NbB<sub>2</sub> was prepared by chemical vapour deposition using the gas mixtures of NbCl<sub>5</sub>, BCl<sub>3</sub> and H<sub>2</sub> on a quartz substrate between the temperatures of 950 and 1200°C, according to the reaction (2.12) (Motojima et al, 1975).



The effects of substrate temperature on the crystal morphology of NbB<sub>2</sub> was examined which resulted in homogeneous films between 950 and 1050°C and pillar crystals between 1050 and 1200°C. Below 900°C and above 1200°C, only the crystalline metallic boron and the contamination of Nb<sub>5</sub>Si<sub>3</sub> were formed, respectively. Thus, the range of 1050-1150°C was determined as the optimum temperature for the growth of needle or pillar crystals of NbB<sub>2</sub>. Furthermore, BCl<sub>3</sub> flow rate and impurity content were affected the morphology and composition of the final products (Motojima et al, 1975).

In order to obtain NbB<sub>2</sub> single crystals, floating zone method has been also applied (Nakano et al, 1981; Otani et al, 1998).

Nakano et al (1981) reported single crystal growth of  $\text{NbB}_2$  by a radio frequency floating zone method using  $\text{NbB}_2$  powders with a purity of 99 %. Feed rods were made by sintering at  $1900^\circ\text{C}$  and crystal growth was carried out in a high frequency heating system under Ar atmosphere. Results showed that over-heating of the molten zone during the growth process caused the formation of boron deficient niobium boride phases such as  $\text{Nb}_3\text{B}_4$ . Single phase  $\text{NbB}_2$  was obtained by avoiding excessive heating of the molten zone (Nakano et al, 1981).

Otani et al (1998) reported the floating zone growth of  $\text{NbB}_2$  single crystals using the powder mixtures of  $\text{NbB}_2$  and B. The mixtures were pressed at 200 MPa into a rod, then the rods were heated at  $1700^\circ\text{C}$  for 30 min in vacuum and the crystal was prepared using a RF heating at 0.5 MPa under Ar atmosphere. By controlling the molten zone composition, the crystals were obtained with free of subgrain boundaries and they did not have preferential growth directions. Furthermore, high temperature hardness of obtained  $\text{NbB}_2$  crystals ( $1110\text{-}1130 \text{ kg/mm}^2$ ) was considerably high as it compared to those of IVA group borides (Otani et al, 1998).

Self-propagating high-temperature synthesis (SHS) of niobium borides with various stoichiometries has been a matter in many studies for years (Takeya et al, 2004; Tsuchida and Kakuta, 2005; Yeh and Chen, 2006a; Yeh and Chen, 2006b; Tsuchida and Kakuta, 2007; Yeh and Wang, 2010).

Takeya et al (2004) investigated the superconducting phase in niobium diborides,  $\text{Nb}_x\text{B}_2$  ( $x=0.67\text{-}1.11$ ), prepared via combustion synthesis from the powder mixture of Nb and B. The initial reaction during the synthesis was stimulated by the arc flame under Ar atmosphere. The results showed that the magnetization curves of  $\text{Nb}_x\text{B}_2$  ( $x=0.67\text{-}1.11$ ) produced by combustion synthesis exhibited broad superconducting transitions (Takeya et al, 2004).

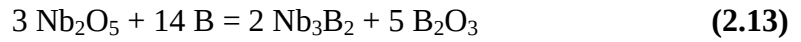
Tsuchida and Kakuta (2005) reported mechanical activation assisted self propagating high-temperature synthesis (MA-SHS) of NbC and  $\text{NbB}_2$  from the powder mixtures of Nb, B and C. Mechanical activation of the powder mixtures were carried out in a planetary ball mill using niobium metals with different particle sizes. Mechanically activated powders were self-ignited in a graphite crucible under air and the exothermic reactions propagated into the reactant powders. NbC and  $\text{NbB}_2$  phases were formed in the samples containing small and large Nb particles after milling for

75 and 60 min respectively and self-ignition in air. However, in both cases Nb phase was still present in the structure. For the comparison, the powder mixtures of Nb, B and C were isothermally heated at 600-1200°C for 60 min under Ar atmosphere. The formation of NbB<sub>2</sub> was occurred at 1000°C and then the formation of NbC with a trace of NbB and Nb<sub>5</sub>B<sub>6</sub> was occurred at 1200°C, in the presence of Nb and C (Tsuchida and Kakuta, 2005). Same authors investigated the effect of the mixing ratio of Nb/B/C and BPR on the MA-SHS of NbC and NbB<sub>2</sub> (Tsuchida and Kakuta, 2007). After milling for 75 min, MA-SHS process was induced in the sample of Nb/B/C=2/2/1 with BPR=1/15 and NbC and NbB<sub>2</sub> were formed, though accompanying with unreacted Nb and a trace of NbO. As the BPR decreased from 1/15 to 1/30 during the milling of Nb, B and C powders, NbB<sub>2</sub> could not be obtained after milling for 150 min and self ignition. Changing the mixing ratio of Nb/B/C strongly affected the obtained phases (Nb or Nb/NbC/NbB<sub>2</sub>) after MA-SHS process (Tsuchida and Kakuta, 2007).

Yeh and Chen (2006b) studied SHS of niobium borides NbB and NbB<sub>2</sub> from elemental compacts. Powder mixtures of Nb and B were mixed in a ball mill for 10 h with molar ratios of Nb:B=1:1 and Nb:B=1:2 for obtaining NbB and NbB<sub>2</sub>, respectively. Milled powders were pressed into cylindrical samples with density ranging from 45 to 60 % of the theoretical maximum density (TMD) and these green bodies were self-ignited in a combustion chamber under Ar atmosphere with preheating temperatures up to 300°C. The combustion temperature was found to increase with an increase in the initial temperature and the green density of the sample. NbB with a small amount of unreacted Nb was obtained from the compacts of Nb:B=1:1. NbB<sub>2</sub> as the dominant phase, along with the presence of minor amounts of Nb<sub>3</sub>B<sub>4</sub> and unreacted Nb was obtained from the compacts of Nb:B=1:2. The composition of final products was independent of the variations in sample green density and preheating temperature in the case of using Nb:B=1:1 or Nb:B=1:2 (Yeh and Chen, 2006b). Same authors were reported the combustion synthesis of various stoichiometries of niobium borides including Nb<sub>3</sub>B<sub>2</sub>, NbB, Nb<sub>5</sub>B<sub>6</sub>, Nb<sub>3</sub>B<sub>4</sub> and NbB<sub>2</sub> from elemental Nb and B powder compacts (Yeh and Chen, 2006a). The experimental conditions reported in above-mentioned study by Yeh and Chen (2006b) were used during SHS process with five different stoichiometric ratios of Nb and B powder blends including Nb:B=3:2, 1:1, 5:6, 3:4 and 1:2. A large amount of

unreacted Nb, NbB and Nb<sub>3</sub>B<sub>4</sub> with a trace amount of NbB<sub>2</sub> were formed in combustion products obtained from the sample compacts with Nb:B=3:2. NbB and Nb<sub>3</sub>B<sub>4</sub> phases with a trace amount of NbB<sub>2</sub> and Nb were formed in combustion products obtained from the sample compacts with Nb:B=5:6. Although the ratios of Nb:B=3:2 and Nb:B=5:6 were used according to the specific compositions of Nb<sub>3</sub>B<sub>2</sub> and Nb<sub>5</sub>B<sub>6</sub> in the Nb-B phase diagram, these phases were not formed in the corresponding combustion products. Therefore, it is claimed that Nb<sub>3</sub>B<sub>2</sub> and Nb<sub>5</sub>B<sub>6</sub> might be kinetically unfavourable. As the initial compositions of Nb:B=1:1 and 1:2 were used, the corresponding stoichiometries of NbB and NbB<sub>2</sub> were obtained as the dominant phase respectively, but Nb was still remained in the structure in both cases. Nb phase was completely converted to niobium borides only in the case of utilizing the reactants of Nb:B=3:4 since Nb<sub>3</sub>B<sub>4</sub> as dominant phase with small amounts of NbB and NbB<sub>2</sub> were obtained in the combustion product. Among the five different initial compositions, the reactant compacts of Nb:B=3:4 had the highest flame propagation rate (Yeh and Chen, 2006b).

Yeh and Wang (2010) reported the combustion synthesis of niobium borides involving the reduction of Nb<sub>2</sub>O<sub>5</sub> by B with different molar ratios of B/Nb<sub>2</sub>O<sub>5</sub> according to the reactions (2.13) and (2.14).



Reactant powders were mixed in a ball mill, cold-pressed into cylindrical specimens and obtained compacts were self-ignited in a stainless-steel chamber under Ar atmosphere. For the samples with a low boron content like Nb<sub>2</sub>O<sub>5</sub>:B=1:5 and 3:16, only NbB was formed as a boride phase with a significant amount of NbO<sub>2</sub>. As the boron content increased in the reactant mixture, NbO<sub>2</sub> phase decreased and NbB<sub>2</sub>, Nb<sub>3</sub>B<sub>4</sub> and NbB phases were obtained in the combustion products indicating an improvement in the degree of borothermic reduction of Nb<sub>2</sub>O<sub>5</sub>. As the molar ratio of Nb<sub>2</sub>O<sub>5</sub> to B decreased from 1:6 to 1:7, dominant boride phase changed from NbB to NbB<sub>2</sub> with an amount of NbO<sub>2</sub>. Full reduction of Nb<sub>2</sub>O<sub>5</sub> and a complete conversion to single-phase NbB<sub>2</sub> was achieved in the samples with the ratios of Nb<sub>2</sub>O<sub>5</sub>:B=1:8.5, 1:9 and 1:10. Thus, the molar ratios of B/Nb<sub>2</sub>O<sub>5</sub> strongly affected the composition of the combustion products. (Yeh and Wang, 2010).

NbB<sub>2</sub> nanorods and NbB<sub>2</sub> nanocrystallites have been prepared by low temperature synthesis in an autoclave using niobium chloride and niobium oxide starting materials (Cai et al, 2005; Ma et al, 2009).

NbB<sub>2</sub> nanorods in the range of 50-60 nm and in the length of up to 600 nm were synthesized in an autoclave at 550-650°C for 12 h using the powder mixtures of NbCl<sub>5</sub> and NaBH<sub>4</sub> in regard of the reaction (2.15) (Cai et al, 2005).



In order to remove the impurities, the products were washed with distilled water and absolute ethanol several times and dried at 60°C for 4 h in vacuum. It was stated that no crystalline products were obtained below 500°C since the NaBH<sub>4</sub> decomposes to BH<sub>3</sub> and NaH above 500°C, according to the reaction (2.16a). Then, NbB<sub>2</sub> was formed by the reaction of NbCl<sub>5</sub> and the gaseous products originated from the reaction (2.16a) (BH<sub>3</sub> and NaH) at 650°C in regard of the reaction (2.16b).



High pressure in the autoclave, coming from the produced BH<sub>3</sub> and H<sub>2</sub>, provided to obtain the crystalline NbB<sub>2</sub> at low temperature (Cai et al, 2005).

Ma et al (2009) reported the preparation of nano-crystalline NbB<sub>2</sub> (30 nm) via a simple inorganic-solvent-thermal route in an autoclave at 650°C for 10 h, using the powder mixtures of niobium oxide, boric acid and magnesium with a mixture of anhydrous sodium chloride and magnesium chloride as inorganic solvent. In order to remove the impurities, the products were washed with absolute ethanol, dilute HCl aqueous solution and distilled water several times and vacuum dried at 60°C for 12 h. It is indicated that the mixture of sodium chloride and magnesium chloride which has a melting point of 425°C acted as a molten salt during the reaction and helped to control the reaction speed and the particles' size. Moreover, high pressure in the autoclave provided by the produced H<sub>2</sub> gas helped to reduce the reaction temperature (Ma et al, 2009).

Ball milling of Nb and B has been applied to obtain NbB and NbB<sub>2</sub> (Morris and Morris, 1991; Iizumi et al, 2006). Recently, mechanochemical synthesis of NbC-NbB<sub>2</sub> and NbB<sub>2</sub> nanocrystallites has been conducted by using Mg, B<sub>2</sub>O<sub>3</sub>, Nb, C and

Al/Mg, B<sub>2</sub>O<sub>3</sub>, Nb powder mixtures, respectively (Torabi et al, 2015; Jafari et al, 2015).

Morris and Morris (1991) examined the mechanical alloying of Nb and B elemental powders to obtain NbB and NbB<sub>2</sub> using a planetary ball mill with a BPR of 4:1 for different milling times ranging between 5 and 80 h.

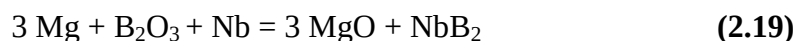
Iizumi et al (2006) reported the mechanochemically assisted preparation of NbB<sub>2</sub> from the powder mixture of Nb and B in 1:2 atomic ratio using a planetary ball mill at 600 rpm with a BPR of 20:1. The effect of ball size on the preparation of NbB<sub>2</sub> was significant since the size of balls changed the milling time required for the formation of NbB<sub>2</sub> with remained Nb and B and single phase without any impurity. For milling with the 5, 9 and 16 mm balls, the starting time of the single phase of NbB<sub>2</sub> formation was 50, 30 and 20 h, respectively. As the diameter of the milling balls increased from 5 to 16 mm, the average particle sizes of NbB<sub>2</sub> obtained after 50 h milling increased from 370 to 980 nm due to the reduced number of contact points between the balls and the powder in longer ball sizes (Iizumi et al, 2006).

Torabi et al (2015) recently studied the mechanochemical synthesis of NbC-NbB<sub>2</sub> nanocomposites by using Mg-B<sub>2</sub>O<sub>3</sub>-Nb-C system. The starting powders were milled in a planetary-ball mill at room temperature with a speed of 500 rpm and with a BPR of 20:1. The initiation of mechanically induced self-sustaining reaction was anticipated for the overall reaction (2.17).



The mechanism of the reaction was explained in the first stage as the reduction of B<sub>2</sub>O<sub>3</sub> by Mg and/or C to produce B and MgO and/or CO. In the next stage, the produced B and C reacted with the Nb and formed NbB<sub>2</sub> and NbC by providing the heat generated from the reduction reaction of B<sub>2</sub>O<sub>3</sub> by Mg. After milling for 3 h and leaching in HCl, NbB<sub>2</sub> and NbC phases were obtained with considerable amount of unreacted Nb. The formation of NbC phase was progressively completed after a longer milling time of 7 h and the intensity of the Nb peak was significantly reduced in the XRD patterns. It was also stated that, unlike the thermal process, there was no formation of magnesium borate phase after mechanochemical synthesis. The sample milled for 7 h and leached in HCl had a powder particle size range below 100 nm (Torabi et al, 2015).

Jafari et al (2015) recently investigated the synthesis of NbB<sub>2</sub> via a mechanochemical route using Al/Mg – B<sub>2</sub>O<sub>3</sub> – Nb system. The starting powders were milled in a planetary-ball mill at room temperature with a speed of 500 rpm and with a BPR of 20:1. Al and Mg were used as reducing agents according to the main reactions (2.18) and (2.19), respectively.



If Al used as reducing agent in the mechanochemical process, only the AlNb<sub>2</sub> intermediate phase was formed even after 60 h of milling. The formation of NbB<sub>2</sub> was achieved after 2.4 h of milling in the case of using Mg as reducing agent. Additionally, beside the reaction product of MgO, magnesium borate was also formed after 2.4 h of milling. However, after 5 h of milling, there was no trace of magnesium borate phase and only the NbB<sub>2</sub> and MgO phases were observed in the XRD patterns. It was stated that the milling process decreased the tendency of magnesium borate formation. After leaching in HCl to remove MgO, single phase NbB<sub>2</sub> was obtained as nanocrystallite having sizes less than 35 nm (Jafari et al, 2015).

### 2.2.3 Sintering techniques of vanadium and niobium borides

Consolidation of transition metal borides has drawn considerable research interest, in view of the mechanical and physical properties of their bulk bodies (Pastor, 1977; Golla and Basu, 2014). Sintering can be broadly classified into two categories including solid-state sintering and liquid-phase sintering (Kang, 2005; Basu and Balani, 2011). Various processing parameters such as starting powders (size distribution and purity), sinter-aid/binder (type and amount) and sintering conditions (heating rate, sintering temperature, sintering time and sintering atmosphere) significantly affect the consolidation process (Kang, 2005; Basu and Balani, 2011; Golla and Basu, 2014). Conventional sintering techniques involve the preparation of powder blends followed by compaction and consolidation at high temperature which can be accomplished by using pressure such as hot pressing (HP) or hot-isostatic pressing (HIP) or without pressure (e.g. pressure sintering in air or inert gas atmosphere) (Kang, 2005; Basu and Balani, 2011). Conventional sintering techniques as well as advanced sintering techniques such as spark plasma sintering

(SPS), microwave sintering, laser sintering etc. have been applied to obtain dense bodies of transition metal borides (Pastor, 1977; Zhang et al, 2008; Basu and Balani, 2011; Silvestroni et al, 2012; Demirskyi et al, 2013). It has been reported that fully dense bodies of  $\text{VB}_2$  and  $\text{NbB}_2$  could hardly be obtained by conventional sintering techniques because sintering of vanadium and niobium borides at temperatures between 2000-2650°C (in the presence of paraffin or PVA binders) resulted in relative densities lower than 80 % (Pastor, 1977).

Even though many studies are available for the fabrication of vanadium and niobium boride powders, sintering processes of them have not been a well discussed topic in the literature. Sintering studies have been mostly carried out in order to investigate superconducting behaviour of niobium borides and they have not reported any microstructural or mechanical properties of bulk products (Yamamoto et al, 2002; Mudgel et al, 2008; Ren et al, 2008). Only the studies conducted by Matsudaira et al (1989) and Sairam et al (2014) reported some mechanical properties (i.e. microhardness, fracture toughness, elastic modulus) of the sintered niobium boride bodies.

Bulk  $\text{NbB}_2$  with a relative density of 98 % and a Vickers micro hardness of 2600  $\text{kg/mm}^2$  was prepared by sintering at 1600°C under a pressure of 4 GPa (Matsudaira et al, 1989).

Yamamoto et al (2002) reported the high-pressure synthesis of superconducting  $\text{Nb}_{1-x}\text{B}_2$  ( $x=0-0.48$ ) phase from the powder mixtures of Nb and amorphous B. Firstly, the amorphous boron was preheated at 800°C for 12 h in a vacuum in order to remove humidity and other impurities. Then, mixed powders were heated at temperatures between 900 and 1300°C in 10 min and sintered in a BN tube under the pressure of 1-5 GPa for 0.5-2 h.  $\text{Nb}_{0.84}\text{B}_2$  phase was obtained by sintering at 1200°C for 0.5 h under 5 GPa and showed superconductivity below 9.1 K.  $\text{Nb}_{0.76}\text{B}_2$  phase showed superconductivity with maximum value of 9.2 K which was sintered at 5 GPa and 1200°C. It is further stated that superconductivity was affected mainly from the composition and the sintering pressure (Yamamoto et al, 2002).

Polycrystalline bulk samples of  $\text{NbB}_{2+x}$  were obtained by sintering in a tubular furnace at 1100°C for 20 h using  $\text{NbB}_2$  and B powders which palletized and encapsulated in iron tubes (Mudgel et al, 2008). Magnetic susceptibility

measurements showed that pure NbB<sub>2</sub> is non-superconductor while non-stoichiometric niobium boride samples for the niobium deficient phases gave diamagnetic signals in the temperature range 8.9 – 11 K (Mudgel et al, 2008).

Another example for sintering of commercial NbB<sub>2</sub> was conducted by using NbB<sub>2</sub> and B or Nb to control Nb/B composition and obtain niobium-, or boron-deficient phases of niobium boride (Ren et al, 2008). Starting materials were mixed, pressed into pellets and sintered in temperatures between 600 and 1400°C for 72 h. XRD analyses of the obtained products showed that systematic shifts of both (002) and (200) occurred with changing sintering temperatures, indicating the changes in c-axis and a-axis. In the case of using appropriate amounts of Nb and B with sintering temperatures between 700 and 1200°C, Nb<sub>0.83</sub>B<sub>2</sub> phase was obtained and it showed superconductivity with T<sub>c</sub> of 9.3 to 9.9 K (Ren et al, 2008).

NbB<sub>2</sub> was synthesized at 1200°C using the stoichiometric amounts of Nb and B powders in regard of the reaction (2.20) and then consolidated at the temperatures in the range of 1700 to 1900°C under load conditions of 30-70 MPa using a spark plasma sintering (SPS) chamber (Sairam et al, 2014).



The formation of single phase NbB<sub>2</sub> was achieved at 1200°C with a short holding period of 1 min due to the applied mechanical pressure which kept elemental powder particles in contact for synthesis reaction. NbB<sub>2</sub> compact with a high density of 97.7 % d<sub>th</sub> was obtained by subsequent heat treatment of the synthesized NbB<sub>2</sub> at 1900°C for 15 min under a pressure of 70 MPa. It is indicated that the sinterability of NbB<sub>2</sub> was significantly improved by increasing heating temperature (from 1700 to 1900°C), holding time (from 1 to 15 min) and mechanical pressure (from 30 to 70 MPa). Vickers hardness, fracture toughness and elastic modulus of the high dense NbB<sub>2</sub> compact was measured as 20.25 GPa, 4 MPa m<sup>1/2</sup> and 539 GPa, respectively (Sairam et al, 2014).

In addition to the above mentioned sintering techniques of niobium borides, some studies have been conducted on the sintering of vanadium-, and niobium boride-based composites:

Tsuchida and Kakuta (2006) studied the fabrication of NbC-NbB<sub>2</sub> composite compacts by spark plasma sintering at 1600-1800°C for 10-30 min under a vacuum

of 6-10 Pa. NbC-NbB<sub>2</sub> precursor powders were prepared by milling of Nb, B and C in a planetary ball mill for 105 min and a subsequent SHS process (MA-SHS). For the comparison, the powder mixtures of Nb/B/C without mechanical activation and the commercial powder mixtures of NbC/NbB<sub>2</sub> were also spark plasma sintered at the same conditions. The highest microhardness value was obtained from the MA-SHS and spark plasma sintered (1800°C, 10 min) sample as HV=19.8 GPa with a relative density of 94 %. On the other hand, NbC/NbB<sub>2</sub> compacts sintered from the powder mixtures without MA-SHS and from the commercial powder mixtures gave the microhardness values of 14.3 and 16.6 GPa, respectively (Tsuchida and Kakuta, 2006).

Malek et al (2013) investigated the electrical discharge machining of (Nb<sub>x</sub>Zr<sub>1-x</sub>)B<sub>2</sub>-SiC composites. Starting materials of NbB<sub>2</sub> and SiC (with 20 vol. %) were milled for 24 h at 70 rpm in ethanol using a multi-directional mixer. Pulsed electric current sintering (PECS) was performed in vacuum (4 Pa) at 2000°C. NbB<sub>2</sub>-SiC composites obtained with a relative density of 98 % exhibited the elastic modulus of 501 GPa and the flexural strength of 206 MPa (Malek et al, 2013).

Demirskyi and Sakka (2014) reported the fabrication of B<sub>4</sub>C-NbB<sub>2</sub> composites by spark plasma sintering (SPS) using NbB<sub>2</sub> and B<sub>4</sub>C powders with different amounts. SPS experiments were performed at 1800-2200°C for 1 min with a pressure of 60 MPa. Composites comprising 60 mol. % NbB<sub>2</sub> showed the highest fracture toughness value of  $7.2 \pm 1.2 \text{ MPa}\cdot\text{m}^{1/2}$ . Microhardness measurements of these composites at the eutectic grains gave the values of HV<sub>0.1</sub>≈35 GPa and HV<sub>1.0</sub>≈27 GPa. On the other hand, NbB<sub>2</sub> grains in the composites exhibited the microhardness values of HV<sub>0.1</sub>≈27 GPa and HV<sub>1.0</sub>≈22 GPa and a fracture toughness value of  $3.4 \pm 0.4 \text{ MPa}\cdot\text{m}^{1/2}$  (Demirskyi and Sakka, 2014).

A patent about the high density metal boride based ceramics reported the sintering of some transition metal borides including VB<sub>2</sub>, VB, NbB<sub>2</sub> and NbB with the additions of binders (0.1-10 wt. % of the total amount) comprising cobalt boride, nickel boride or iron boride and carbides or carbonitrides (0.1-10 wt. % of the total amount) comprising Ti, Zr, W and C (Watanabe et al, 1991). The mixed powders were packed into graphite dies and were sintered under the condition of 200 kg/cm<sup>2</sup> pressure in a vacuum at 1500°C for 60 min. The obtained ceramics exhibited good wear resistance

and high density which could be used for cutting tools, especially wood-working tools (Watanabe et al, 1991).

### **2.3 Mechanical Alloying and Milling-Assisted Methods**

Mechanical alloying (MA) is a powder processing technique that allows production of homogeneous materials starting from blended powders. MA can be simply defined as a method for the utilization of powder mixing with the grinding balls to cause milling of powders (Suryanarayana, 2001). MA and milling-assisted routes date back to the early history, since first attempts were done to obtain fire by friction and more recent data on the ignition of certain solid state reactions which initiated by mechanical means (Boldyrev, 1986; McCormick and Froes, 1998). Mechanical milling has been traditionally used for blending powders and crushing rocks and has been routinely used in powder metallurgy and mineral processing industries (Zhang, 2004).

MA has been accepted as a potential non-equilibrium processing technique (Koch et al, 1983). The formation of amorphous phases was achieved by mechanical grinding of several compounds such as Y-Co, Ni-Nb, Ni-Zr, Cu-Ti etc. (Koch et al, 1983; Suryanarayana, 2001; Zhang, 2004). For some systems, such as Al-Mg or Al-Ti, it was found that other metastable phases (e.g.  $\text{Al}_{12}\text{Mg}_{17}$ ,  $\text{Al}_3\text{Ti}$ ) formed in the alloyed powders instead of the formation of amorphous alloys (Zhang, 2004). Thus, syntheses of a variety of stable and metastable phases and amorphous alloys by using mechanical alloying/milling processes have been investigated for years (Suryanarayana, 2001). Figure 2.8 shows the steps of powder evolution during MA indicating the five typical stages of ball milling of ductile powder mixtures. It was emphasized that the mixture of the initial powders finally becomes homogeneous and the elements are mixed on an atomic scale due to the flattening, welding and fracturing mechanism during milling (Balaz et al, 2013).

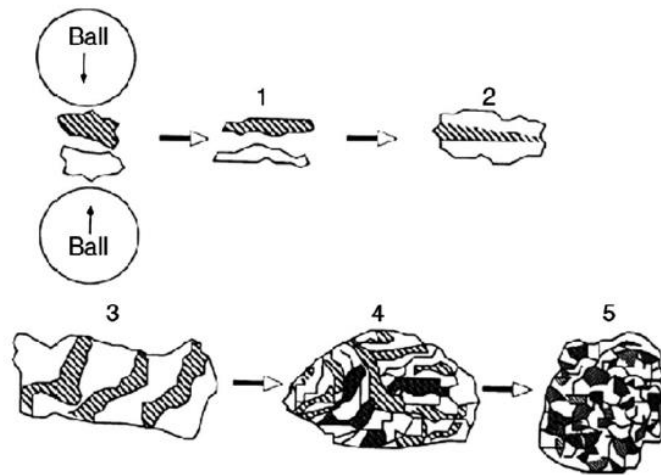


**Figure 2.8 :** Steps of powder evolution during mechanical alloying: 1 – initial powders, 2 – flattering, 3 – welding, 4 – 3D welding and fracturing, 5 – stable end product, adapted from Balaz et al, 2013.

Moreover, it has been shown that it is possible to produce pure metals, nanocomposites and a variety of commercial materials at room temperatures or much lower temperatures by the effect of mechanical activation (Suryanarayana, 2001). There have been numerous reports showing that an intermetallic compound or silicide or carbide powder can be produced by high-energy mechanical milling of a mixture of elemental powders. Furthermore, it has been established that for producing nanocrystalline powders, mechanical milling is one of the major techniques because the grain size of the powder particles continues to decrease until it reaches a minimum level (Zhang, 2004). Further studies have been carried out on the metal–ceramic composites and nanocomposite powders: Mechanical milling allowed the incorporation of the metal and the ceramic phases into each powder particle, as shown schematically in Figure 2.9 (Zhang, 2004; German, 2005).

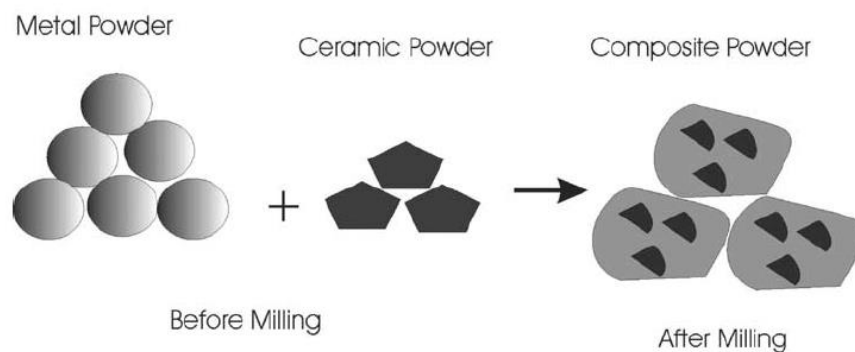


**Figure 2.9 :** The formation of composite powder after high-energy mechanical milling of metal and ceramic powders, adapted from Zhang, 2004.

MA and milling-assisted routes have been also applied on the fabrication of superalloys and heat-resistant alloys in order to achieve a homogeneous dispersion of brittle nanoparticles in the metal matrix. The items manufactured after consolidation of the milled powders had an improved strength and they were termed as dispersion strengthened alloys (Balaz et al, 2013). Formation of an amorphous phase on milling a mixture of pure Zr (ductile) and  $\text{NiZr}_2$  intermetallic (brittle) powder particles is a typical example of this type of system (Suryanarayana, 2001).

In addition, since 1980s, syntheses of a variety of products and advanced materials have been investigated by using mechanochemical processes among milling-assisted methods. Mechanochemical synthesis is a milling process of powders involving reduction reactions and/or chemical reactions between the reagents (Suryanarayana, 2001). In recent years, more than 1500 scientific papers have been published every year in the field of mechanochemistry (Sopicka-Lizer, 2010). Mechanochemical methods show some promise for the synthesis of different materials such as lithium ion batteries, hydrogen storage materials, photocatalysts, etc. (Huot et al, 2013).

Some other terms are also used in the literature on MA: Reaction (or reactive ball) milling, cryomilling, rod milling, mechanically activated annealing (M2A), double mechanical alloying (dMA), and mechanically activated self-propagating high-temperature synthesis (MASHS). Mechanically activated annealing (M2A) has been developed to obtain different refractory materials. This is a process that combines short MA duration with a low-temperature isothermal annealing (Suryanarayana, 2001).

Consequently, typical current and potential applications of MA products can be summarized as below (Zhang, 2004; Balaz et al, 2013):

- Amorphous alloy powders and alloy powders with other metastable phases
- Nanostructured materials
- Pure metals
- Dispersion strengthened superalloys and heat-resistant alloys
- Metal-ceramic composites and nanocomposite powders
- Novel phases, carbides, nitrides, silicides, borides etc.

- Hydrogen storage materials, lithium ion batteries, catalysts, magnetic materials etc.

In this dissertation, mechanochemical synthesis and mechanically activated annealing processes are used as ball milling-assisted solid state methods to obtain borides and their composite powders.

### 2.3.1 Ball milling

Ball milling or mechanical milling utilize mixing of elemental powders along with the grinding balls to cause milling of powders. This process leads to a particle size reduction due to repeated crushing of powder particles between balls moving at high speeds and includes extensive deformation and subsequent fracturing (Basu and Balani, 2011). Thus, repeated deformation, fracturing and cold welding of particles occur in a highly energetic ball mill. The particles become homogeneous at the atomic level after a time period (German, 1994). Figure 2.10 shows the ball-powder-ball collision of powder mixtures during a mechanical milling process. By a series of collisions of balls with each other and with the reactor walls, a fraction of powder is trapped between colliding surfaces of the milling tools and submitted to a mechanical load at relatively high strain-stress leading to work hardening and fracture (Figure 2.10) (Gilman and Benjamin, 1983; Suryanarayana, 2001).

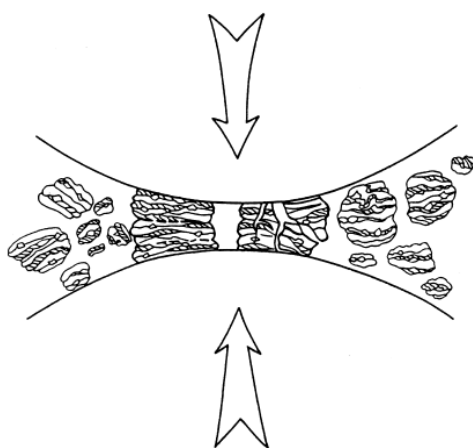


**Figure 2.10 :** Ball-powder-ball collision of powder mixtures during mechanical milling process, adapted from Suryanarayana, 2001.

The powders are cold worked, welded and fragmented repeatedly, resulting in powders with a uniform atom distribution. The clean surfaces come into contact and weld together and particle size increases (Fecht, 2002). At this stage, powder

particles have a characteristically layered structure. During continued deformation, the fatigue failure mechanism and fragmentation of fragile flakes causes work hardening and fracture. And at this stage, fracturing becomes dominant over cold welding. A steady-state equilibrium is reached when a balance is achieved between the rate of welding and the rate of fracturing (Suryanarayana, 2001).

High-energy mills have different working regimes such as compression, shear and impact. The principles of the most frequently applied mills are schematically shown in Figure 2.11 (Balaz et al, 2013). Different motions of the balls are observed in Figure 2.11 which can be described as cascading, falling, cataracting or centrifugal.

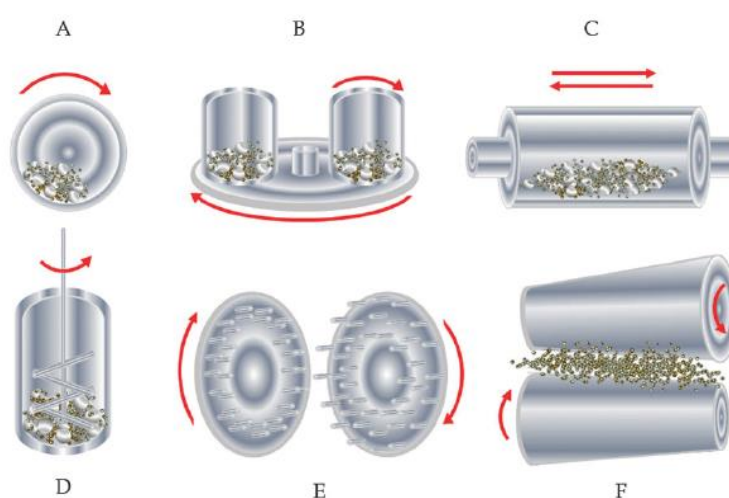


**Figure 2.11 :** Types of mills for high-energy milling: A – ball mill, B – planetary mill, C – vibration mill, D – attritor (stirring ball mill), E – pin mill, F – rolling mill, adapted from Balaz et al, 2013.

Amongst the different high-energy milling equipment, the types of mills generally used for MA are mixer/mills, planetary ball mills and attritors (stirred ball mills). The main differences of these mills are their capacity, speed of operation, efficiency of milling and the functions for controlling the milling temperature and contamination of powders (Balaz, 2008). Figure 2.12(a), (b) and (c) show the examples of the mixer/mill (SPEX<sup>TM</sup> 8000D Dual Mixer/Mill), planetary ball mill (Fritsch<sup>TM</sup> Pulverisette) and attritor (Union Process Model 01-HD attritor), respectively.



(a)



(b)



(c)

**Figure 2.12 :** Examples of the mill types: (a) Mixer/mill (SPEX<sup>TM</sup> 8000D Dual Mixer/Mill), (b) Planetary ball mill (Fritsch<sup>TM</sup> Pulverisette) and (c) Attritor (Union Process Model 01-HD attritor).

SPEX mills consist of one vial or two vials and make back and forth motion several thousands per minute (Suryanarayana, 2001). Planetary ball mills are characterized by the planet-like movements of its vials with two relative motions: a rotary motion around the mill axis and a planetary motion around the vial axis (Balaz, 2008). Attritor mills consist of a cylindrical grinding chamber with a centrally mounted vertical shaft having horizontal arms radiating from it and the grinding media (Soni, 2001).

Various types of mills are available for wet or dry grinding processing which can be used with different sizes and capacities (from 2 g to 100 kg). On the other hand, commercial mills are much larger in size than the mills described above and can process several hundred kilograms at a time (with a capacity up to 1250 kg) (Suryanarayana, 2004). Figure 2.13 shows some examples of the ball mills for the

commercial production designed by different companies. High-kinetic rotor ball mills (Figure 2.13(a)) were designed and reflect almost one decade of specialization in MA, high energy milling and reactive milling. These ball mills have grinding units with capacities up to 1850 kg (Url-3).

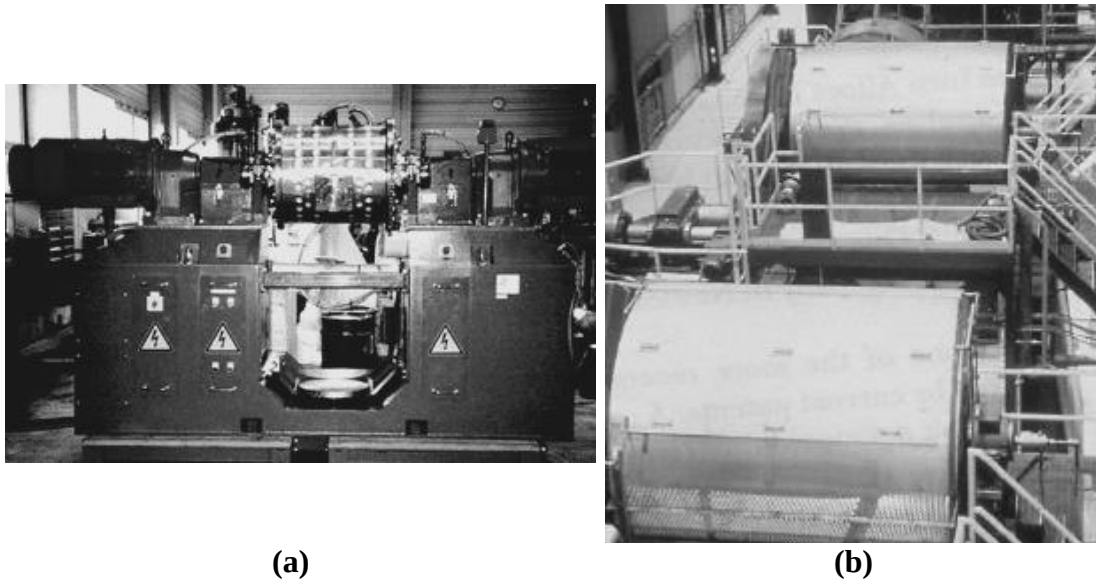


**Figure 2.13 :** Examples of the commercial production size ball mills: (a) Zoz GmbH Simoloyer ball mill, (b) Inco Alloys International ball mills.

Different types of vial materials are available including hardened steel, alumina, tungsten carbide, zirconia, stainless steel, silicon nitride, agate, plastic and methacrylate (Suryanarayana, 2004). For the mixing and homogenization of the powders, different kind of balls (stainless steel, WC,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  etc.) is used (Basu and Balani, 2011).

MA and ball milling-assisted techniques are complex processes and highly affected by a number of processing parameters. Hence, optimization of these variables is needed to obtain the desired product phase and/or microstructure. Some of the important parameters are (Suryanarayana, 2001; Suryanarayana, 2004):

- Type of mill,
- Milling rate,
- Milling time,
- Milling atmosphere,
- Ball-to-powder weight ratio (BPR),

- Material of milling media,
- Extent of filling the milling vial,
- Temperature of milling,
- Process control agent (PCA)

Type of mill can be chosen by considering the type and quantity of powders and the final constitution required. The maximum milling rate varies widely for different types of mills and milling rate affects the collision energy during milling (Suryanarayana, 2001). It is significant to choose the appropriate milling time because when time is longer than required, the level of contamination increases and undesirable phases form (Suryanarayana, 2001; Balaz, 2008). Milling atmosphere is also important to avoid oxidation and/or contamination of the powders so loading is usually carried out inside atmosphere-controlled glove boxes. The BPR affects considerably the time needed to have a particular phase because a high BPR provides an increase in the number of collisions per unit time and consequently more energy is transferred to the powder particles. Thus, shorter times are required with higher BPR but at the same the usage of big amounts of balls increase the contamination coming from the balls. In order to prevent cross contamination, material of milling media (milling chamber, vial and balls) can be made of the same material as the powder. The shape of the vial and the density and size of the balls are also important parameters. The milling vial should not overfill and generally about 50 % of the vial space is left empty because enough space should be given to the balls and the powder particles to move around freely in the milling vial. Local temperature between balls during collision and overall temperature of the vial occur during milling process which affect the formation of phases. In some studies, the temperature of milling was intentionally changed by electrical heating or liquid nitrogen. Furthermore, PCA can be used during milling because they preferentially adsorb onto the interfaces and minimize the cold welding by lubricating effect (Suryanarayana, 2001).

### **2.3.2 Mechanochemical synthesis**

Mechanochemical processing is the term applied to the powder process in which chemical reactions and phase transformations take place due to application of mechanical energy (Suryanarayana, 2004). The term of mechanochemistry has been

widely used for materials synthesis initiated by mechanical forces since it was first proposed by Ostwald (1887). The definition of Heinicke is widely accepted: “Mechanochemistry is a branch of chemistry which is concerned with chemical and physico-chemical transformations of substances in all states of aggregation produced by the effect of mechanical energy” (Heinicke, 1984; Balaz et al, 2013).

Mechanism of mechanochemical synthesis includes the processes of MA and reactive milling which start after mechanical activation of reagents. Mechanical activation enhances the reactivity of powders by enlarging the surface area or accelerating the reaction. Mechanical deformation of crystalline structures causes the local structural stimulations and creates non-equilibrium thermodynamic conditions which increase chemical reactivity significantly (Heinicke, 1984; Gutman, 1998). The impact energy obtained in the processes of plastic deformation, fracture and friction is converted into other forms of energy such as structural defects, broken bonds and other types of excess energy. These energies accumulate in the system and a new and active state of the substances is obtained and chemical reactivity of the powders rises (Chen et al, 1997). Moreover, the necessity for diffusion through the product layer is eliminated due to the increase in the surface areas of powder particles. The fresh contact surfaces allow reactions to occur at lower temperatures without any external applied heat. Alternatively, reduction in diffusion distances can considerably reduce the reaction temperature as a result of the particle refinement (Suryanarayana, 2001).

Most of the mechanosynthesis reactions studied in recent years have been according to the displacement reaction (2.21), where a metal oxide (MO) is reduced by a more reactive metal (reductant, R) to the pure metal M. In addition to the oxides, metal chlorides and sulphides have also been reduced to pure metals by this way (Suryanarayana, 2004).



Figure 2.14 schematically shows the chemical reaction occurring between two components (MO and R) in the mechanochemical reactions. All solid-state reactions involve the formation of a product phase at the interface of the component phases. The product phases (M and RO) form at the interface between the oxide (MO) and the reductant (R) and prevent further reaction from occurring since the reactants are

not in contact with each other. In other words, the reaction interface continuously decreases during the course of the reaction. The interface can be defined as the nominal boundary surface between the reactants, and so reaction kinetics is slow. The reaction rates are determined by the diffusion rates of the reactants through the product phase which acts as a barrier. Therefore, elevated temperatures are required to achieve reasonable reaction rates. Reactions characterized by a large negative free energy change are thermodynamically feasible at room temperature. Thus, increase in the rate of solid-state reaction is very important aspect of mechanochemistry with respect to the interaction between the reactants (Suryanarayana, 2004; Balaz et al, 2013).

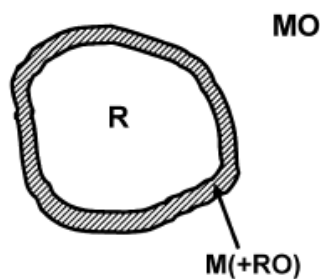


**Figure 2.14 :** Chemical reaction occurring between two components (metal oxide, MO and reductant, R) in the mechanochemical reactions, adapted from Suryanarayana, 2004.

Two different reaction kinetic mechanisms are possible depending on the milling conditions: Gradual transformation or self-propagating reaction. In the first type of kinetic mechanism, a slowly developing reaction with each collision occurs and reactions proceed slowly up to the point where the processes turn to time controlled mechanism. The formation reactions of products develop gradually (Wieczorek-Ciurowa et al, 2010). In the second type of kinetic mechanism, the reaction enthalpy is sufficiently high and needs a critical milling time for the propagating reaction to be initiated. The temperature increases slowly at the beginning and after a period of milling, temperature climbs suddenly, which confirmed the fact that ignition has occurred. The reduction reaction occurs only beyond this time, reaction takes place within seconds (Wieczorek-Ciurowa, 2010).

The kinetics of mechanochemical reactions can be changed by tailoring the previously explained ball milling parameters. In addition to these parameters, relative proportion of the reactants is also another important parameter for mechanochemical

synthesis. About 10-15 % stoichiometric excess of the reducing agent has been generally used in most of the research investigations. The reactive reductant powders can be exposed to partial surface oxidation so that excess amount is used to compensate this missing amount (Suryanarayana, 2004).

### **2.3.3 Mechanically activated annealing**

The term *mechanical activation* is explained as a process which causes an increase in reaction ability of a substance by mechanical treatment (Balaz, 2008). Butyagin (1984) explained the effect of mechanical energy on the solids by three main aspects: Structural disordering, structural relaxation and structural mobility. Structural relaxation plays an important role in mechanical activation and solids reveal different times of relaxation after interrupting the action of mechanical forces (Butyagin, 1984). By this theory, the states whose relaxation time is less than reaction time does not influence the reactivity of activated solids and some long-lived states (e.g., surface area) may regard as having major influence. Therefore, mechanical activation is a multi-step process with changes in energetic parameters (Balaz, 2008). The term mechanical activation unites the four processes, namely, the accumulation of defects, amorphization, the formation of metastable polymorphous forms and chemical reaction (Boldyrev and Tkacova, 2000). Juhasz (1998) subdivided the processes under the influence of mechanical activation into primary and secondary processes: primary ones generally increase the reactivity of substance (increase of internal and surface energy, increase of surface area, decrease of the coherence energy of solids) and secondary processes (aggregation, adsorption, recrystallization) occur spontaneously and may complete after milling (Juhasz and Kollath, 1993; Juhasz, 1998).

Mechanical activation of milled material is achieved by increase of both the specific surface energy and the elastic strain energy. The surface free energy can be dissipated by agglomeration of new fracture surface or adsorption of environmental gaseous species and moisture. The relaxation processes for bulk activation are heating, fracturing of the brittle material, crystallographic lattice rearrangements, chemical reactions between adjoin points and imperfections (Boldyrev, 1986; Juhasz and Kollath, 1993; Lin, 1998). The elastic strain energy transforms into lattice defects such as point defects (vacancies), linear defects (dislocations), planar defects

(stacking faults or sub-crystallite interfaces) and volumetric defects (structural disordering) (Lin, 1998).

The term *annealing* is explained as a heat treatment process and during annealing, residual stresses are relieved by recovery and recrystallization stages (Thümmeler and Oberacker, 1993). Annealing process can be carried out at high or low temperatures in an atmosphere furnace (in air or in the presence of an inert gas) or a vacuum furnace. The aims of the annealing are to soften the powder and to reduce the residual amount of oxygen, carbon and/or nitrogen from the powder (Upadhyaya, 2002). The additional use of reducing atmospheres such as hydrogen or dissociated ammonia further lowers the oxygen content and prevents re-oxidation. Partial sintering of the powder particles occurs during annealing processes which is resulted in the particle size enlargement. In most cases this is an unintended consequence of annealing necessitating a subsequent crushing of the annealed product agglomerates. The heat treatments are therefore performed at temperatures as low as possible, to minimize sintering and to allow for a subsequent mild comminution without significant strain hardening (Thümmeler and Oberacker, 1993).

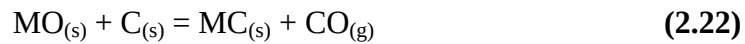
*Mechanically Activated Annealing* (M2A) is a process that combines short mechanical milling times with a low-temperature isothermal annealing. Short milling process provides the mechanical activation of the powder particles and subsequent annealing enables the activated particles to react at lower temperatures than thermodynamically required. The combination of these two steps has been found to be effective in producing different refractory materials (Suryanarayana, 2004). One of the first examples of this process was the formation of  $\text{MoSi}_2$  particles which were achieved by milling of Mo and Si for 2 h and subsequent annealing at 800°C for 2-24 h (Gaffet and Malhouroux-Gaffet, 1994). The conditions of mechanical activation (type of mill, milling time, milling rate etc.) and annealing (annealing temperature, annealing time, annealing atmosphere etc.) are the significant parameters affecting the M2A process (Suryanarayana, 2004).

In this dissertation, milling-assisted carbothermal reduction process was used to obtain boride-carbide composite powders which is based on the main principles of M2A routes.

### 2.3.3.1 Milling-assisted carbothermal reduction process

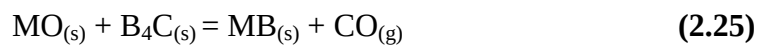
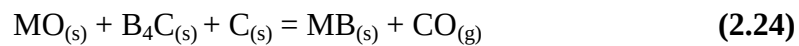
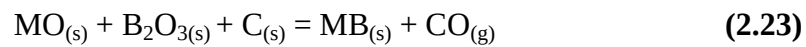
Milling-assisted production of the refractory materials has been applied by using subsequent reactive annealing and SHS techniques. In these studies, first step is milling of the starting materials by various ball milling techniques to activate the powder mixtures and the second step is subsequent solid-state reaction of the activated particles at relatively low or low temperatures or by SHS techniques (Gaffet and Malhouroux-Gaffet, 1994; Gauthier et al, 1999). Based on this principle, carbothermal production technique has been also utilized to obtain refractory materials by using a ball milling step prior to the solid-state reaction (Gauthier et al, 1999).

Carbothermal reduction process can be explained according to the overall reaction (2.22) based on the reduction of metal oxide by carbon (C) resulting in the formation of metal carbide (MC) and carbonmonoxide (CO) as gas reaction product (Berger et al, 1999).



The carbothermal reduction of the metal oxides is characterized by a very contradictory relationship between thermodynamics and kinetics including the mass transfer, reaction rate, the formation of oxide intermediates etc. (Berger et al, 1999).

Carbothermal reduction process for obtaining metal borides (MB) can be done by using a corresponding metal oxide (MO) and a carbon source such as C or B<sub>4</sub>C in regard of the reactions (2.23) through (2.25) (Maeda et al, 1994; Kang and Kim, 2007; Qiu et al, 2012).



The preparation of boride-based ceramic powders at a comparatively low temperature without the need for post-synthesis treatment using the carbothermal method may provide a significant improvement in the fabrication process (Kang and Kim, 2007; Qiu et al, 2012; Balcı et al, 2012; Hassan et al, 2013). Some limited studies exist in the current literature relating the simultaneous synthesis of NbC and NbB<sub>2</sub> from elemental powder mixtures of Nb, B and C by a mechanical activation-

assisted SHS process (Tsuchida and Kakuta, 2005; Tsuchida and Kakuta, 2007). Due to the combination of the excellent properties of  $\text{NbB}_2$  and  $\text{NbC}$ , fine and homogeneous microstructures of these ceramics can be a potential precursor powder for the development of  $\text{NbB}_2$ -based dense bodies. Furthermore, the existence of carbides in the boride matrix drives the formation of a protective layer during oxidation and enhances the oxidation resistance of borides at high temperatures. This is significant for high-temperature structural applications of the composites, where oxidation resistance is highly demanded (Gasch et al, 2004). Moreover, it is well known that *in situ* techniques involve chemical reactions that result in the formation of new phases, and this provides a strong matrix reinforcement bond that is not easy to obtain in *ex situ* processes (Gilliard et al, 2014).



### 3. EXPERIMENTAL PROCEDURE

The experimental procedure of this dissertation comprises the identification of raw materials, the mechanochemical and milling-assisted carbothermal synthesis of the powders, the consolidation of the purified powders via pressureless sintering and spark plasma sintering techniques and characterization investigations carried out on the powders and sintered products. Moreover, FactSage<sup>TM</sup> thermodynamic calculations are presented at the end of this chapter.

#### 3.1 Raw Materials

The use of low-cost starting materials is one of the major purposes of this dissertation in order to suggest economically-efficient techniques for obtaining high-tech boron products. Therefore, in all experiments, low-cost oxide raw materials were used as corresponding metal and boron sources. Table 3.1 shows the characteristics of the raw materials used in the experiments. The synthesis of vanadium and niobium borides and their composite powders were originated from their oxide powders such as V<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub>. B<sub>2</sub>O<sub>3</sub> powders were used as a native boron source (Eti Mine, Turkey) for the formations of boride phases. Mg powders were also native source (MME, Turkey) and used in the mechanochemical synthesis experiments as a strong metallic reducing agent. Graphite (C) powders were used in the milling-assisted carbothermal reduction processes as a carbon reductant. Figure 3.1 shows the SM images of the raw materials. The images of all raw materials were captured by using a Zeiss<sup>TM</sup> Discovery.V12 Stereomicroscope (SM) coupled with a Zeiss<sup>TM</sup> Axiocam ERc5s high resolution digital camera.

**Table 3.1 :** Raw materials used in the experiments.

| Raw material                   | Provided from            | Purity (%) | Average Particle Size (μm) |
|--------------------------------|--------------------------|------------|----------------------------|
| V <sub>2</sub> O <sub>5</sub>  | Alfa Aesar <sup>TM</sup> | 99.6       | 300                        |
| Nb <sub>2</sub> O <sub>5</sub> | Alfa Aesar <sup>TM</sup> | 99.5       | 20                         |
| B <sub>2</sub> O <sub>3</sub>  | Eti Mine                 | 98         | 470                        |
| Mg                             | MME                      | 99.7       | 145                        |
| C                              | Alfa Aesar <sup>TM</sup> | 99         | 45                         |

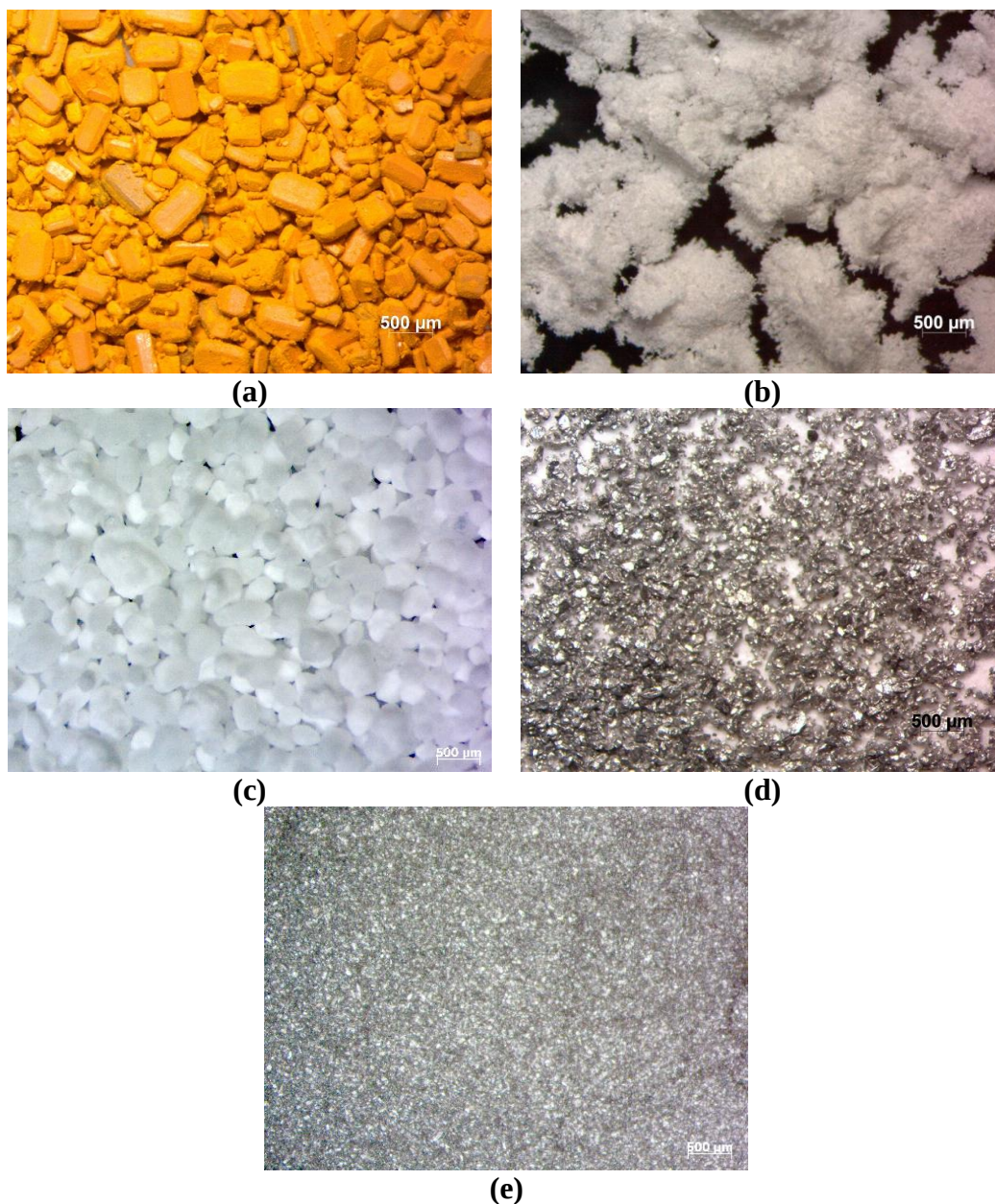


**Figure 3.1 :** SM images of the raw materials: (a)  $V_2O_5$ , (b)  $Nb_2O_5$ , (c)  $B_2O_3$  (d) Mg and (e) C.

The phases of all raw materials were identified using a Bruker<sup>TM</sup> D8 Advanced Series X-ray diffractometer (XRD) with  $CuK\alpha$  (1.54060 Å) radiation in the  $2\theta$  range of 10-80° with 0.02° steps at a rate of 2°/min. International Centre for Diffraction Data (ICDD) powder diffraction files were utilized for the crystalline phase identification of the raw materials. The XRD patterns of the raw materials are illustrated in Figure 3.2(a) through Figure 3.2(e). Figure 3.2(a), (b), (d) and (e) respectively present the crystalline peaks of  $V_2O_5$  (ICDD Card No: 01-070-8747, Bravais lattice: primitive orthorhombic,  $a=1.150$  nm,  $b=0.355$  nm,  $c=0.435$  nm),  $Nb_2O_5$  (ICDD Card No: 01-071-0336, Bravais lattice: primitive orthorhombic,

$a=0.617$  nm,  $b=2.917$  nm,  $c=0.393$  nm), Mg (ICDD Card No: 35-0821, Bravais lattice: primitive hexagonal,  $a=b=0.329$  nm,  $c=0.521$  nm) and C (ICDD Card No: 056-0159, Bravais lattice: primitive hexagonal,  $a=b=0.246$  nm,  $c=0.671$  nm), without any trace of impurities. Figure 3.2(c) shows the characteristic peak structure of amorphous  $B_2O_3$  with the presence of small  $H_3BO_3$  (ICDD Card No: 01-072-3608) peak at  $2\theta=28^\circ$ . The reason of the presence of small amount of  $H_3BO_3$  in the structure of  $B_2O_3$  is due to the humidity arised from the handling of powders in laboratory atmosphere.

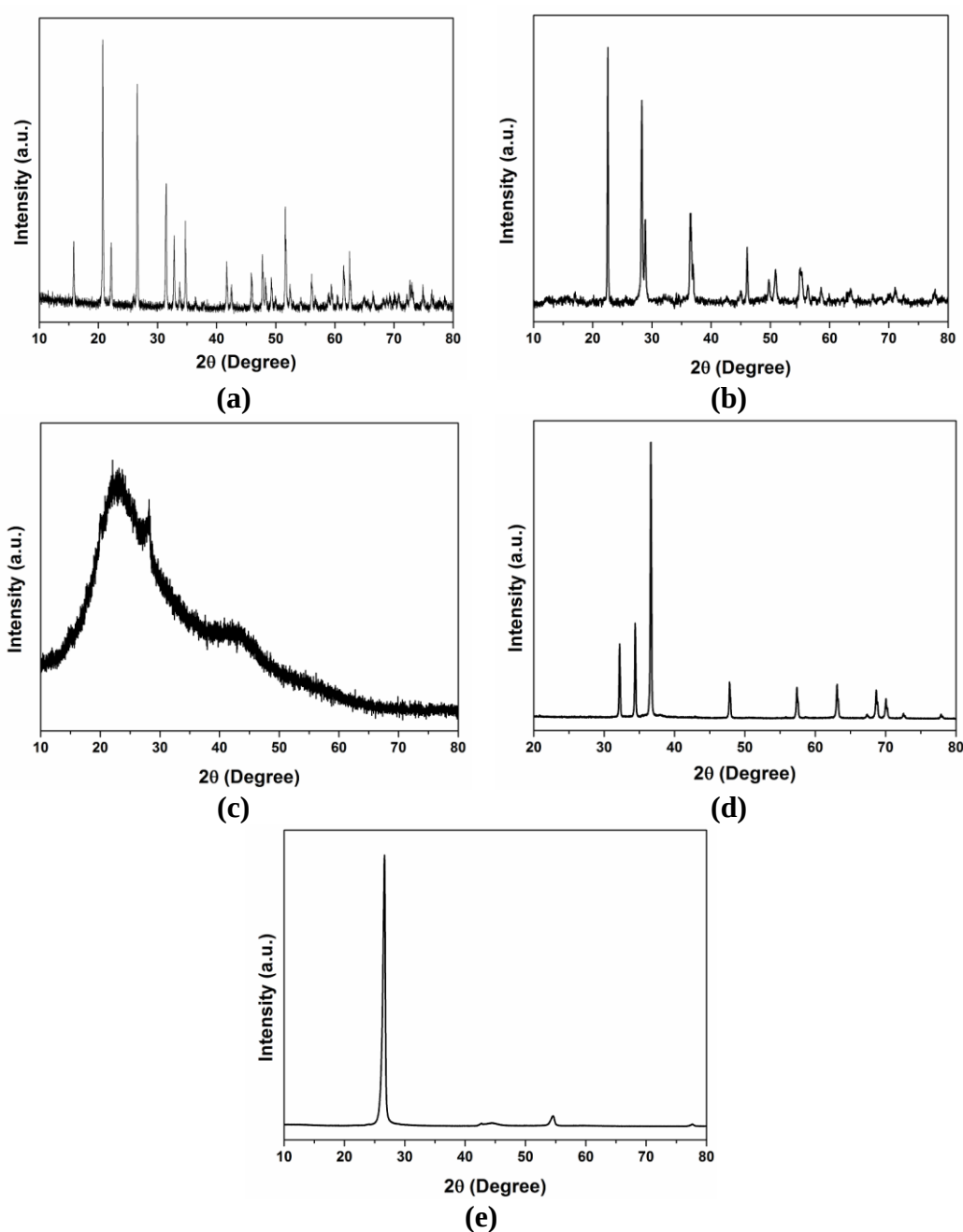


**Figure 3.2** : XRD patterns of the raw materials: (a)  $V_2O_5$ , (b)  $Nb_2O_5$ , (c)  $B_2O_3$  (d) Mg and (e) C.

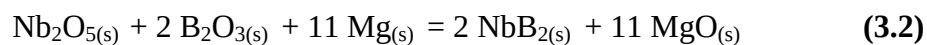
In addition to the above mentioned raw materials, Co sintering agent was used in the consolidation experiments. Co powders were provided from Eurotungstene® and have a purity of 99.7 % and a particle size of 28 µm.

### 3.2 Synthesis and the Consolidation of the Powder Blends

One of the major aims of this dissertation is to find an effective technique for preparing metal borides that could overcome the limitations of conventional productions and represent the advantages of time and energy savings, simplicity and high-purity products. Milling-assisted solid-state methods utilized in this dissertation involve inducing chemical reactions in powder blends at room temperature or lower temperatures than thermodynamically required. The synthesis of vanadium and niobium boride powders were utilized using two different techniques including mechanochemical reactions using oxide raw materials/Mg reductant and milling-assisted carbothermal reactions using oxide raw materials/C reductant. The consolidation of the purified powders was carried out by different sintering techniques such as cold pressing/pressureless sintering (without or with Co addition) and spark plasma sintering (SPS).

#### 3.2.1 Mechanochemical synthesis of the powders and their purification

Powder blends containing stoichiometric and/or stoichiometric excess amounts of the reactants for synthesizing vanadium and niobium boride powders were prepared according to the ideal reactions given in (3.1) and (3.2).

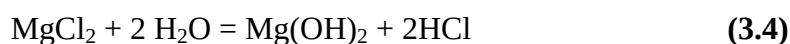
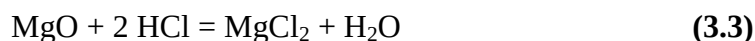


Stoichiometric excess amounts (25, 50 and 75 wt. %) of reducing agent (Mg) and boron source ( $\text{B}_2\text{O}_3$ ) were used in the synthesis of borides along with stoichiometric amounts in order to reveal the effects of amount of reactants on the properties of mechanochemically synthesized products. Non-milled (0 h) powders were blended and homogenised in a WAB™ T2C Turbula blender for 1 h and hereafter referred to as-blended powders. For mechanical milling experiments, powder batches of 6 g each were prepared and mechanical milling times varied up to max. 20 h.

Mechanical milling was conducted using a high-energy ball mill (Spex™ 8000 D Mixer/Mill) with a milling rate of 1200 rpm. Milling was performed with a ball-to-

powder weight ratio (BPR) of 10:1 using hardened steel balls (6 mm diameter) in a hardened steel vial (50 ml capacity). Sample handling was carried out in a glove box (Plaslabs<sup>TM</sup>) under a purified Ar atmosphere (Linde<sup>TM</sup>, in purity of 99.999 %). The milling vials were evacuated to about  $10^{-2}$  Pa and back filled with Ar gas in the glove box to prevent surface oxidation and contamination of powder blends from atmospheric conditions.

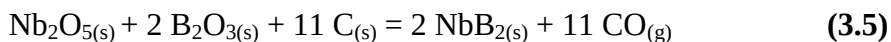
Following milling experiments, selective HCl (Merck<sup>TM</sup>, in concentration of 37 %) leaching was applied on the products in order to remove undesired MgO phase and other impurities (especially Fe, Cr and Ni) released from the milling media. Leaching was carried out with a 4 M HCl solution under the effect of ultrasonic stirring (Bandelin<sup>TM</sup> Sonorex) for 15 min with a solid/leachant ratio of 1 g/10 cm<sup>3</sup>. The intermediate products were leached using excess HCl molarity (4 M) with the intention of obtaining pure boride powders. The molarity of commercial HCl solution in concentration of 37 % was calculated as 12.076 mol/L. 1 M HCl leaching solution can be obtained by mixing 83 ml HCl solution ( $1/12.076 = 0.083$  L) with 917 ml distilled water. Thus, the leaching solutions used in the experiments were prepared by the help of these calculations. MgO reacted with the leaching solution according to the reactions (3.3) and (3.4).



At the end of leaching treatment, the solutions containing insoluble solids were subjected to repeated centrifuging in a Hettich<sup>TM</sup> Rotofix 32A centrifuge with a rotation speed of 3500 rpm for 30 min, repeated decanting, repeated washing with distilled water for several times and lastly remained solids were dried under air in a FN 500 stove at 120°C for 24 h. Leach solutions decanted from the solids after each centrifuging-decanting-washing treatment were collected into a volumetric flask for the subsequent instrumental analyses. Besides, all the collected leach solutions which belonged to different products were equated to 100 ml with distilled water for the correct comparison.

### 3.2.2 Milling-assisted carbothermal production of the powders

Powder blends containing stoichiometric amounts of the reactants were prepared according to the overall reaction (3.5).



Stoichiometric excess amount (100 wt. %) of reducing agent (C) was used in the synthesis of niobium borides/carbides along with stoichiometric amounts in order to reveal the effects of amount of reducing agent on the final properties of carbothermal products. Non-milled (0 h) powders were blended and homogenised in a blender for 1 h and hereafter referred to as-blended powders. For mechanical milling experiments, powder batches of 6 g each were prepared and mechanical milling times varied up to max. 5 h. Equipment and application for mechanical milling experiments were the same as utilized in the mechanochemical synthesis experiments.

Annealing of the powders was conducted using a horizontal tube furnace (Protherm<sup>TM</sup>). The as-blended and milled powders were placed in an alumina boat and then were heated at a rate of 10°C/min to the temperatures of 1300 and 1400°C and annealed for 12 h under a flowing Ar atmosphere (Linde<sup>TM</sup>, in purity of 99.999 %). After reaction, the product was slowly cooled to room temperature with a rate of 10°C/min. Any post-treatment process was not applied for the purification of the powders because intermediate product (CO) was easily removed from the system in gas phase during carbothermal reaction.

### 3.2.3 Consolidation of the purified powders via different sintering techniques

After powder production, optimized conditions of obtaining pure niobium and vanadium boride powders were determined and selected powders in high qualities were consolidated by cold pressing/pressureless sintering (PS, with or without Co addition) and spark plasma sintering techniques (SPS). Table 3.2 lists the synthesis and sintering conditions of the optimized samples selected for the consolidation experiments of vanadium and niobium borides. In order to reveal the effect of mechanical milling (MM) time on the bulk properties, mechanochemically synthesized niobium boride powders prepared using different times (5 and 9 h) were consolidated by PS and SPS. Furthermore, in order to show the effect of sintering aid on the bulk properties, niobium boride powders in optimized conditions were

pressureless sintered by the use of metallic Co sinter additive (2 and 5 wt. % of the total powder amounts). Thus, the effects of synthesis conditions, presence/absence of metallic sintering aid and different sintering techniques on the bulk properties were investigated. Bulk products were hereafter referred as the sample names given in Table 3.2.

**Table 3.2 :** Synthesis and sintering conditions of the optimized samples selected for the consolidation experiments of vanadium and niobium borides.

| Starting Materials                                                | Powder Preparation                                  | Sintering Conditions                                       | Sample Name |
|-------------------------------------------------------------------|-----------------------------------------------------|------------------------------------------------------------|-------------|
| Nb <sub>2</sub> O <sub>5</sub> -B <sub>2</sub> O <sub>3</sub> -Mg | MM for 5 h and HCl leaching                         | Cold pressing and pressureless sintering at 1500°C for 4 h | N5-PS       |
| Nb <sub>2</sub> O <sub>5</sub> -B <sub>2</sub> O <sub>3</sub> -Mg | MM for 9 h and HCl leaching                         |                                                            | N9-PS       |
| Nb <sub>2</sub> O <sub>5</sub> -B <sub>2</sub> O <sub>3</sub> -Mg | MM for 5 h and HCl leaching, 2 wt.% Co              |                                                            | N5-2CoPS    |
| Nb <sub>2</sub> O <sub>5</sub> -B <sub>2</sub> O <sub>3</sub> -Mg | MM for 5 h and HCl leaching, 5 wt.% Co              |                                                            | N5-5CoPS    |
| V <sub>2</sub> O <sub>5</sub> -B <sub>2</sub> O <sub>3</sub> -Mg  | MM for 7 h with 50 wt. % excess Mg and HCl leaching |                                                            | V7-PS       |
| Nb <sub>2</sub> O <sub>5</sub> -B <sub>2</sub> O <sub>3</sub> -Mg | MM for 5 h and HCl leaching                         | Spark plasma sintering at 1500°C for 15 min under 60 MPa   | N5-SPS      |
| Nb <sub>2</sub> O <sub>5</sub> -B <sub>2</sub> O <sub>3</sub> -Mg | MM for 9 h and HCl leaching                         |                                                            | N9-SPS      |
| V <sub>2</sub> O <sub>5</sub> -B <sub>2</sub> O <sub>3</sub> -Mg  | MM for 7 h with 50 wt. % excess Mg and HCl leaching |                                                            | V7-SPS      |

For the cold pressing/pressureless sintering, powders were compacted in a 10 ton capacity MSE<sup>TM</sup> MP-0710 uni-axial hydraulic press under a pressure of 800 MPa. Thus, green bodies owning cylindrical preforms with a diameter of ~6.3 mm were obtained after cold pressing (CP). The green bodies were sintered at 1500°C for 4 h in a Linn<sup>TM</sup> HT-1800 high temperature controlled atmosphere furnace with a heating and cooling rate of 10°C/min under Ar gas (N5-PS, N9-PS, V7-PS). Co powders were added to the pure powders by milling for 5 min in a high-energy ball mill (Spex<sup>TM</sup> 8000 D Mixer/Mill). Thus, pure niobium boride powders with the addition of metallic Co were also consolidated at the same conditions (N5-2CoPS, N5-5CoPS) as the powders prepared without sintering aid. Figures 3.3(a) through 3.3(f) illustrate the SM images of the some green bodies and bulk structures of vanadium and niobium borides consolidated without or with the use of metallic Co sinter additive. As seen from Figure 3.3(d) through 3.3(f), sintered compacts do not have any shape deformation in their upper and lateral surfaces after CP and PS and they conserved their dimensional structures. As the green bodies (Figure 3.3(a)-(c)) and

the sintered structures (Figure 3.3(d)-(f)) are compared to each other, there is an considerable decrease in the diameter sizes of the samples after sintering which indicates a shrinkage in the sample volumes and a significant densification during PS.

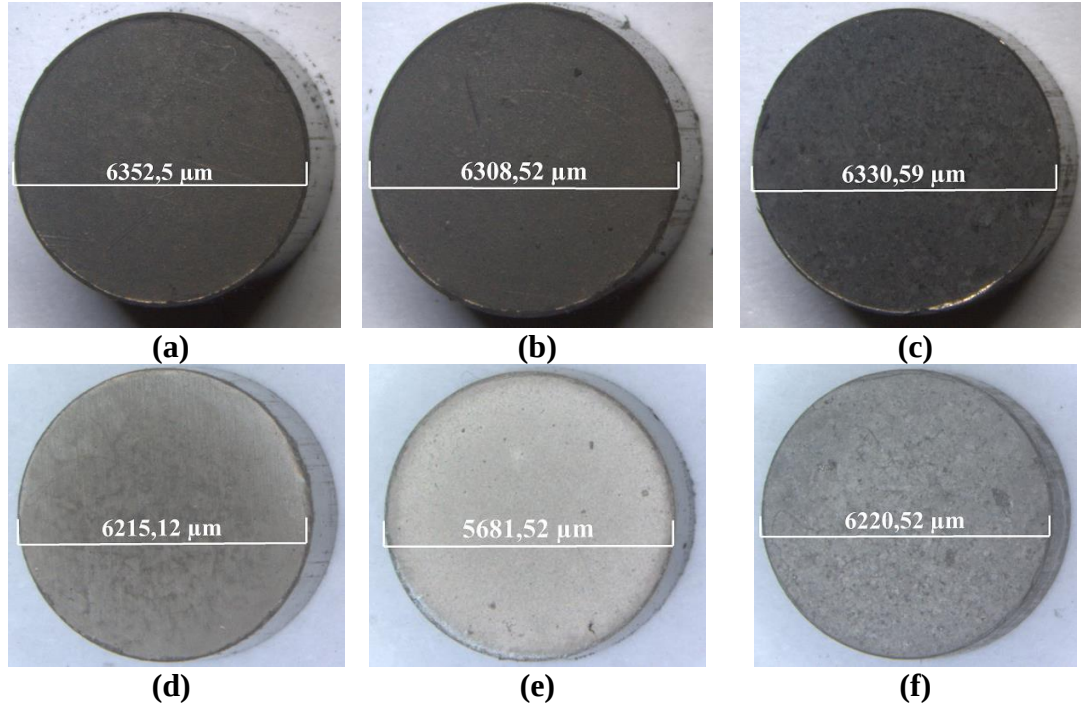


**Figure 3.3 :** SM images of the some green bodies (a, b and c) and sintered structures (d, e and f) of vanadium and niobium boride samples: (a),(d) N5-PS, (b),(e) N5-2CoPS and (c),(f) V7-PS.

Spark plasma sintering (SPS) experiments were conducted using a FCT Systeme™ HP D 25 SPS equipment. Powders were loaded in a graphite die with an inner diameter of 20 mm and sintered at 1500°C for 15 min with heating and cooling rates of 100°C/min under an applied holding pressure of 60 MPa (N5-SPS, V7-SPS). Another niobium boride powder prepared by different milling time was also spark plasma sintered at the same conditions to investigate the effect of milling time (N9-SPS).

### 3.3 Characterization Investigations of the Powders and Sintered Products

Characterization investigations conducted on the powders in this dissertation comprise the detailed microstructural analyses, the determination of phases, thermal properties and particle sizes of both the milled and final powders. Moreover, purity and density values of the final powders are identified by various methods. Phase and microstructural properties and densities of the sintered products are also determined

comprehensively. Furthermore, mechanical properties of the selected samples are reported in terms of microhardness, wear resistance, wear tracks, elastic modulus, indentation curves and fracture toughness of the bulk products.

### **3.3.1 Characterization investigations of the powders**

X-ray diffraction (XRD) investigations of the as-blended, milled, leached or annealed powders and of the sintered samples were performed in a Bruker<sup>TM</sup> D8 Advanced Series powder diffractometer with CuK $\alpha$  ( $\lambda=0.154$  nm) radiation in the  $2\theta$  range of  $10-90^\circ$  incremented at a step size of  $0.02^\circ$  at a rate of  $2^\circ/\text{min}$ . The International Center for Diffraction Data<sup>®</sup> (ICDD) powder diffraction files were utilized for the identification of crystalline phases. Average crystallite sizes and lattice strains of the carbothermally synthesized powders were determined utilizing Bruker-AXS<sup>TM</sup> TOPAS V3.0 software based on the modified Scherrer's formula (Suryanarayana and Norton, 1998). The most intense diffraction peaks of the phases were fitted according to the Lorentzian profile by applying fundamental parameters approach. The phase amounts in the synthesized powders were identified by the semi-quantitative Rietveld method. The images of as-blended, milled, leached and annealed powders were captured by using a Zeiss<sup>TM</sup> Discovery.V12 Stereomicroscope (SM) coupled with a Zeiss<sup>TM</sup> Axiocam ERc5s high resolution digital camera. Particle size measurements were conducted on the milled and leached powders using a Microtrac<sup>TM</sup> Nano-flex particle size analyzer (PSA). In order to prevent agglomeration of the particles, powders were homogenized in a Bandelin Sonopuls<sup>TM</sup> ultrasonic homogenizer for 15 min using distilled water as aqueous media prior to particle size measurements. The thermal properties of the as-blended, milled and final powders were examined using a TA<sup>TM</sup> Instruments SDT Q600 Differential Scanning Calorimeter (DSC)/Thermogravimetric Analyser (TGA). DSC/TGA experiments were conducted in an alumina crucible up to a heating temperature of  $1400^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$  under an Ar atmosphere. After DSC analyses, some heated powders were subjected to additional XRD analyses to detect the obtained phases (hereafter referred as DSC samples). To reveal the free C content in the carbothermally produced samples, the obtained powders were oxidised at  $800^\circ\text{C}$  for 15 min and the free C content was calculated from the weight difference. Fourier transform infrared (FTIR) spectra were recorded for some powders at wave number values ranging between  $1000$  and  $4000\text{ cm}^{-1}$  with a

resolution of  $4\text{ cm}^{-1}$  and sample and background scan time of 24 scans/min using the KBr pellet technique by a Bruker<sup>TM</sup> Alpha-T spectrometer equipped with a DRIFT module.

Microstructural characterisations of the powders were carried out using an FEI – Quanta FEG 250 Scanning Electron Microscope (SEM) coupled with an energy-dispersive X-ray spectrometer (EDX) - energy dispersive spectrometer (EDS) and also using a JEOL JEM-ARM200CFEG UHR Transmission Electron Microscope (TEM). To obtain a flat surface and clearly reveal the phase distribution, SEM/EDX analysis was carried out on compacted pellets of the milled powders. For SEM analysis of the powders, the specimens of the powders were prepared by following the procedure of dissolving the powders in the ethanol (Merck<sup>TM</sup>, in purity of 99.9 %), syringing them onto a base plate, drying them in air and coating their surfaces with a thin layer of gold using a Polaron<sup>TM</sup> SC7620 Sputter Coater to enhance their conductivities. For TEM analysis, the particles were dispersed in the ethanol and a drop of it was taken on a porous carbon film supported on a copper grid and dried in a vacuum oven.

The densities of the final powders were measured by a Micromeritics<sup>TM</sup> AccuPyc II 1340 gas pycnometer in a  $1\text{ cm}^3$  sample chamber at room temperature using He gas (Linde<sup>TM</sup>, in purity of 99.996 %) as the displacement medium. Density result of each powder product includes the arithmetic mean of ten successive measurements and standard deviations. The specific surface areas of some powders were measured using the Brunauer–Emmet–Teller (BET) method by a Quantachrome Autosorb-1 MP device, at  $150^\circ\text{C}$  by degassing under  $\text{N}_2$  gas for 5 h and by absorbing with  $\text{N}_2$  (for analysis) and He (for reference) gases. In the mechanochemical synthesis experiments, the amounts of Mg and Fe elements in the leach solutions after the purification by leaching processes were analysed in a Perkin Elmer<sup>TM</sup> 1100B atomic absorption spectrometer (AAS). Fe impurities worn off from the milling vial and balls were analysed in the leach solution by AAS and in the purified powders by vibrating sample magnetometer (VSM). Magnetic measurements of the milled and purified powders were conducted by a vibrating sample magnetometer (VSM) at room temperature under DC-biased magnetization between 0 and 8000 Oe.

### 3.3.2 Characterization investigations of the sintered products

Microstructural characterisations of the sintered products were carried out using the XRD technique at the same conditions as those of powders, the Hitachi<sup>TM</sup> TM-1000 scanning electron microscope (SEM) operating at 15 kV and the optical microscope (OM, Nikon, Eclipse). The densities of the sintered samples were measured in ethanol using the Archimedes method and the results were reported as the arithmetic means of three different measurements taken from the same sample. In order to obtain scratch-free mirror finish for SEM analyses, Vickers microhardness measurements and reciprocating sliding wear tests, all sintered samples were subjected to a typical metallographic preparation procedure. Sintered samples were hot-mounted in a Struers<sup>TM</sup> LaboPress-1, ground and polished in a Struers<sup>TM</sup> Tegrapol-15 instrument.

Vickers microhardness measurements of the sintered samples were conducted using a Shimadzu<sup>TM</sup> HMV Microhardness Tester under a load of 200 g for 15 s. Microhardness test result for each sample includes the arithmetic mean of twenty successive indentations and standard deviations. All sintered samples were subjected to reciprocating sliding wear tests at room temperature in a laboratory atmosphere by a Tribotech<sup>TM</sup> Oscillating Tribotester using a 6 mm alumina ball under an applied force of 4 N, with a sliding speed of 6 mm/s and a stroke length of 2 mm for a total sliding distance of 20 m. Wear tracks of all the sintered samples were imaged by using the Hitachi<sup>TM</sup> TM-1000 SEM and examined by a Veeco<sup>TM</sup> Dektak 6M Stylus Profilometer. Wear test results in terms of wear volume loss ( $WVL = (\pi/4) * \text{width} * \text{depth} * \text{length}$ ) values are the arithmetic mean of three different measurements for each sample. Relative wear resistance values were calculated as the ratio of highest wear volume loss to the wear volume of each sample. Depth-sensing indentation measurements of the selected samples were performed at a peak load of 250 mN, using a CSM<sup>TM</sup> International MHT SN 06-0212 instrumented Vickers indenter. The applied load versus penetration depth curves were obtained at a loading and unloading rate of 500 mN/min with a holding time of 2 s at the peak load. In addition, elastic modulus of the samples was obtained according to the Oliver-Pharr method (Oliver and Pharr, 1992). The fracture toughness of the selected samples was estimated from the cracks obtained by the Vickers indentation technique (Shimadzu<sup>TM</sup> HMV Microhardness Tester) using 2 kg load for 15 s. The indentation

mark was evaluated with the relation given in equation (3.6), where  $K_{IC}$  is the fracture toughness ( $\text{MPam}^{1/2}$ ),  $a$  is 1/2 of indentation diagonal length ( $\mu\text{m}$ );  $c$  is 1/2 of crack length ( $\mu\text{m}$ ) and  $H$  is Vickers hardness ( $\text{Hv}$ ) (Niihara et al, 1982).

$$K_{IC} = 0.203 (c/a)^{-3/2} Ha^{1/2} \quad (3.6)$$

Vickers hardness values determined in this study were used in the calculation of fracture measurement. Fracture surface analysis (e.g. indentation cracks) was carried out by a Leica<sup>TM</sup> ICC50HD OM.

### 3.4 Thermodynamic Calculations

Thermodynamic calculations were theoretically conducted by FactSage<sup>TM</sup> 6.2 thermochemical software. The proposed reaction mechanisms in this dissertation for the mechanochemical and milling-assisted carbothermal reactions are representatively explained for the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  and  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-C}$  systems, respectively. Figure 3.4 gives the standard Gibbs free energy changes ( $\Delta G^\circ$ ) of the reactions (3.2) and (3.5) emphasizing the difference between the magnesiothermal and the carbothermal reactions. As seen from Figure 3.4, the reaction (3.2) has large negative standard free energy changes (between -2610 and -900 kJ) in the temperature range of 0-2000°C. This means that reaction (3.2) takes place spontaneously and therefore it is thermodynamically feasible at room temperature and above. Similarly, according to the data obtained for  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  system, the reaction (3.1) has also large negative standard free energy changes (between -2900 and -1020 kJ) in the temperature range of 0-2000°C. The values of standard Gibbs free energy changes at room temperature for the reactions (3.1) and (3.2) are respectively -2850 and -2600 kJ, which promote that the formation of  $\text{VB}_2$  is comparably easier than that of  $\text{NbB}_2$ . On the other hand, the reaction (3.5) has a positive standard free energy change of 2147.1 kJ at room temperature, and it has negative free energy changes at temperatures above 1200°C. The value of the Gibbs free energy change decreases from -26.4 to -550.6 kJ as the temperature increases from 1200 to 1500°C, indicating that the mentioned reaction is thermodynamically not feasible at temperatures between 25 and 1200°C, and hence it takes place spontaneously if the temperature is increased beyond 1200°C.

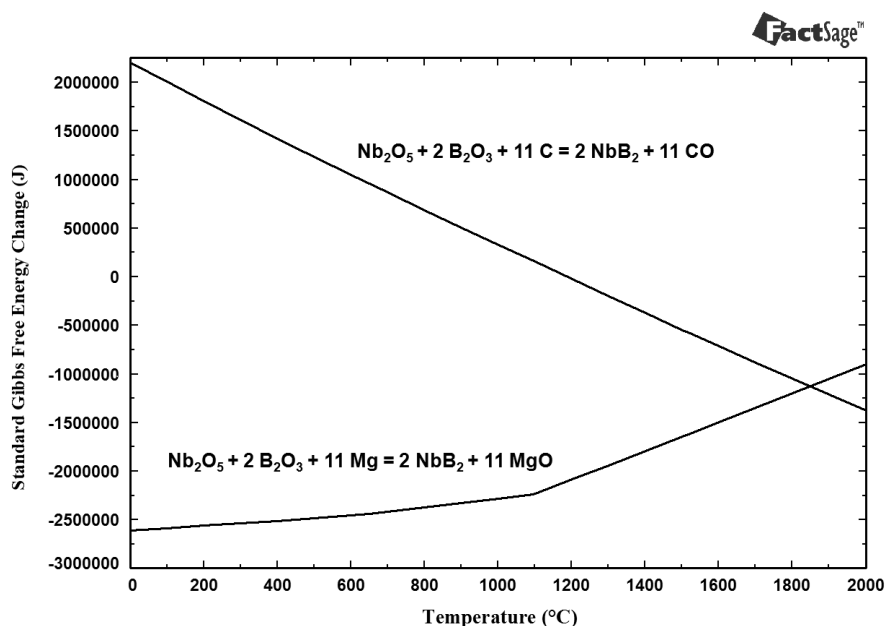
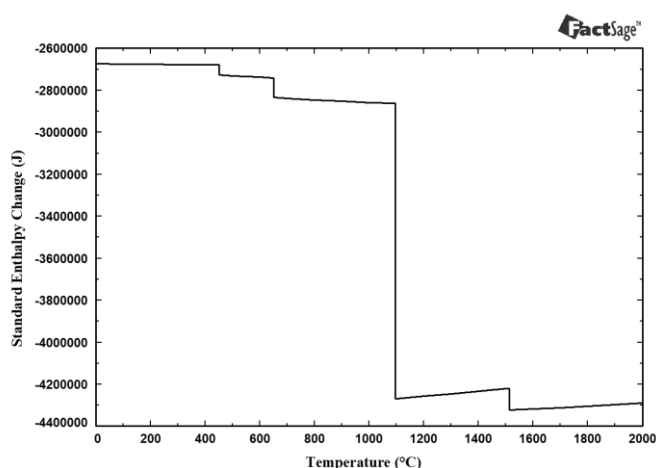
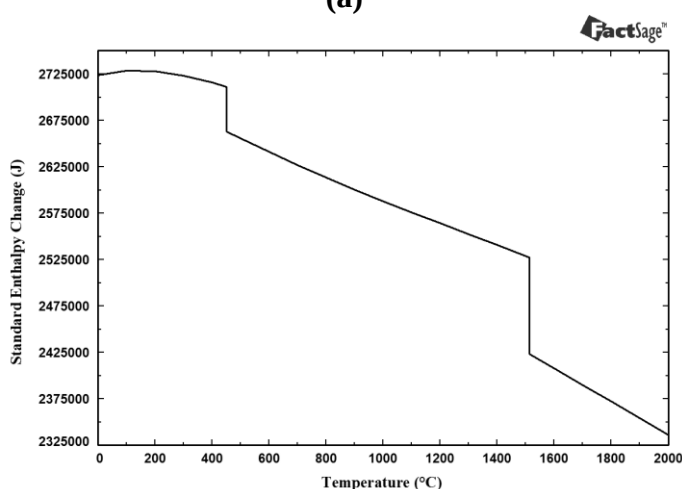


**Figure 3.4 :** Standard Gibbs free energy changes of the reactions (3.2) and (3.5) varying according to the temperature.

Figure 3.5 gives the standard Gibbs free energy changes ( $\Delta G^\circ$ ) of the reactions (3.2) and (3.5) varying according to the temperature up to 2000°C. Figure 3.5(a) presents the declines of enthalpy at 450, 650, 1095 and 1512°C indicate the melting of  $B_2O_3$ , the melting of Mg, boiling of Mg and melting of  $Nb_2O_5$ , respectively. Large negative standard enthalpy changes of the reaction (3.2) implies that large amount of heat is released during the occurrence of them. It can be predicted that the vial temperature significantly increases during milling in the presence of Mg due to the exothermic reaction. On the other hand, Figure 3.5(b) presents the positive standard enthalpy changes and only shows the declines of enthalpy at 450 and 1512°C which respectively correspond to the melting of  $B_2O_3$  and  $Nb_2O_5$ . Consequently, the comparison of the standard Gibbs free energy changes and standard enthalpy changes of the  $Nb_2O_5$ - $B_2O_3$ -Mg and  $Nb_2O_5$ - $B_2O_3$ -C systems reveals the effect of different reducing agents (Mg or C) on the thermodynamical behaviours.



(a)



(b)

**Figure 3.5 :** Standard enthalpy changes varying according to the temperature: (a) reaction (3.2) and (b) reaction (3.5).

The reaction products for the  $V_2O_5$ - $B_2O_3$ -Mg,  $Nb_2O_5$ - $B_2O_3$ -Mg and  $Nb_2O_5$ - $B_2O_3$ -C systems were thermodynamically predicted by varying the temperature up to 2000°C. Magnesiothermal systems give only the reaction products of corresponding diboride and MgO at the all temperatures whereas carbothermal products highly affect from the temperature changes. The molar amounts of the reactants and products varying according to the reaction temperature (up to 2000°C) were calculated for the  $Nb_2O_5$ - $B_2O_3$ -C system according to the reaction (3.5) at stoichiometric conditions (Figure 3.6). On the basis of the thermodynamic predictions, the reaction between  $Nb_2O_5$ ,  $B_2O_3$  and C requires a temperature above 900°C because the reaction products  $NbC_{(s)}$  and  $CO_{(g)}$  are formed at this temperature after the initiation of  $B_2O_3$  melting at 400°C. NbC is present at 1000°C with a maximum amount of 2 moles from consuming approximately 7 moles of C, and NbC

linearly diminishes at temperatures above 1400°C. Meanwhile, NbB<sub>2</sub> starts to occur at 1400°C, and its amount linearly increases up to the temperature of 1500°C and reaches a constant and maximum amount of 2 moles. The C reactant and NbC product completely disappear at 1500°C, meaning that the NbB<sub>2</sub> phase emerges from the reaction between 2 moles of NbC, 4 moles of C and 2 moles of B<sub>2</sub>O<sub>3</sub>. The formation of NbC consumes the majority of the reducing agent. Direct synthesis of the NbB<sub>2</sub> phase from Nb<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub> and C-containing powder blends, in other words, direct carbothermal reduction of Nb<sub>2</sub>O<sub>5</sub> and B<sub>2</sub>O<sub>3</sub>, is not possible due to the higher affinity of C to Nb rather than that of boron. In addition, only the NbB<sub>2(s)</sub> and CO<sub>(g)</sub> phases exist above 1500°C as constant reaction products owing to the participation of NbC in the reduction process its complete conversion.

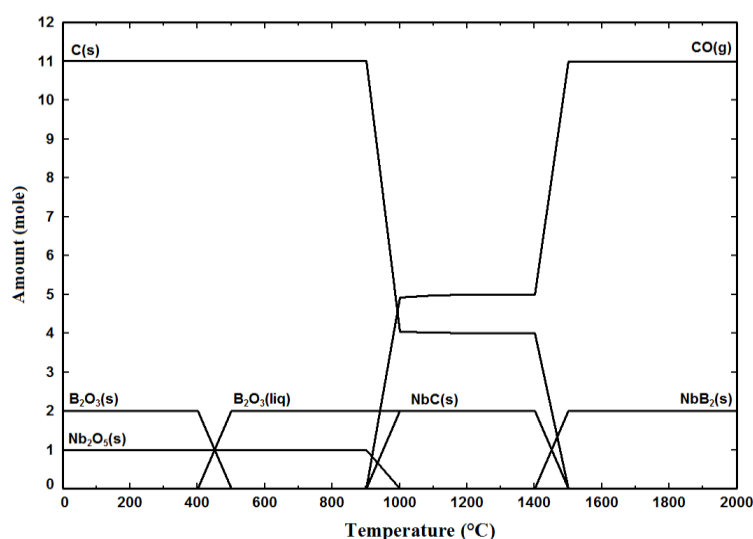


**Figure 3.6 :** Molar amounts of reactants/products of the reaction (3.5) varying according to the temperature.

Molar amounts of the reactants/products of the reaction (3.5) varying according to the C amount were calculated at the temperature where NbB<sub>2</sub> reaches its maximum value (1500°C) and given in Figure 3.7. As seen from Figure 3.7, the maximum values of the reaction products NbB<sub>2(s)</sub> and CO<sub>(g)</sub> can be obtained by using 20 moles C. This means that about 100 % stoichiometric excess amount of C reducing agent is needed for the complete reduction of Nb<sub>2</sub>O<sub>5</sub> and B<sub>2</sub>O<sub>3</sub>. Therefore, additional experiments were carried out by using 100 wt. % stoichiometric excess amount of C in order to show the effects of C amounts on the reaction products.

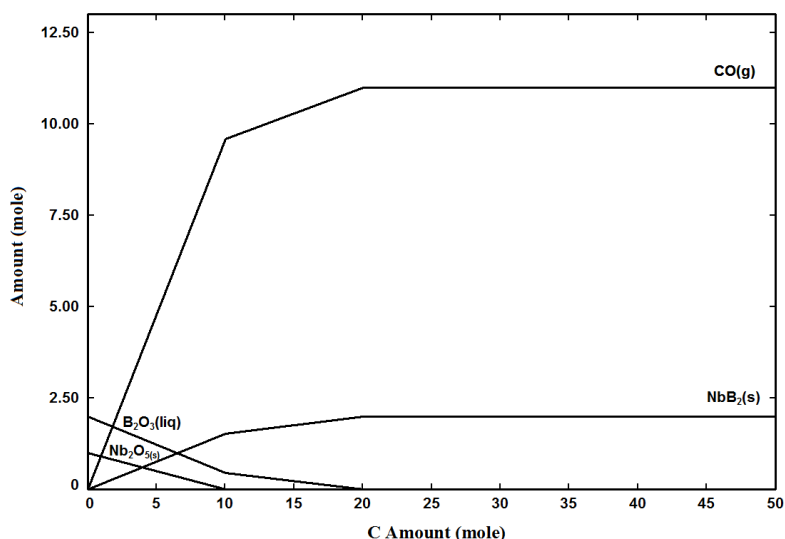


**Figure 3.7 :** Molar amounts of reactants/products of the reaction (3.5) at 1500°C varying according to the C amount.

Since the products of the magnesiothermal reactions do not affect from the temperature change, molar amounts of the reactants/products were predicted according to the varying  $B_2O_3$  or Mg amount. As a representative of the magnesiothermal systems, the molar amounts of the reactants and products varying according to the  $B_2O_3$  or Mg amount were calculated for the  $V_2O_5$ - $B_2O_3$ -Mg system according to the reaction (3.1) at 1400°C, which was the maximum applicable value in the DSC analyses (Figure 3.8). As seen from Figure 3.8(a), the maximum value of the  $VB_{2(s)}$  reaction product can be obtained by using 5 moles  $B_2O_3$  which means 150 wt. % stoichiometric excess amount of  $B_2O_3$ . However, at this value,  $Mg_3B_2O_{6(s)}$  is also formed at its maximum amount and  $Mg_2B_2O_{5(s)}$  starts to form. Therefore, 50 wt. % stoichiometric excess amount of  $B_2O_3$  was selected to use in the experiments in order to show the effects of boron source. As seen from Figure 3.8(b), the maximum values of the reaction products  $VB_{2(s)}$  and  $MgO_{(s)}$  can be obtained by using 15 moles Mg. This means that about 50 % stoichiometric excess amount of Mg reducing agent is needed for the complete reduction of  $V_2O_5$  and  $B_2O_3$ . Therefore, additional experiments were carried out by using 25 and 50 wt. % stoichiometric excess amounts of Mg in order to show the effects of Mg amounts.

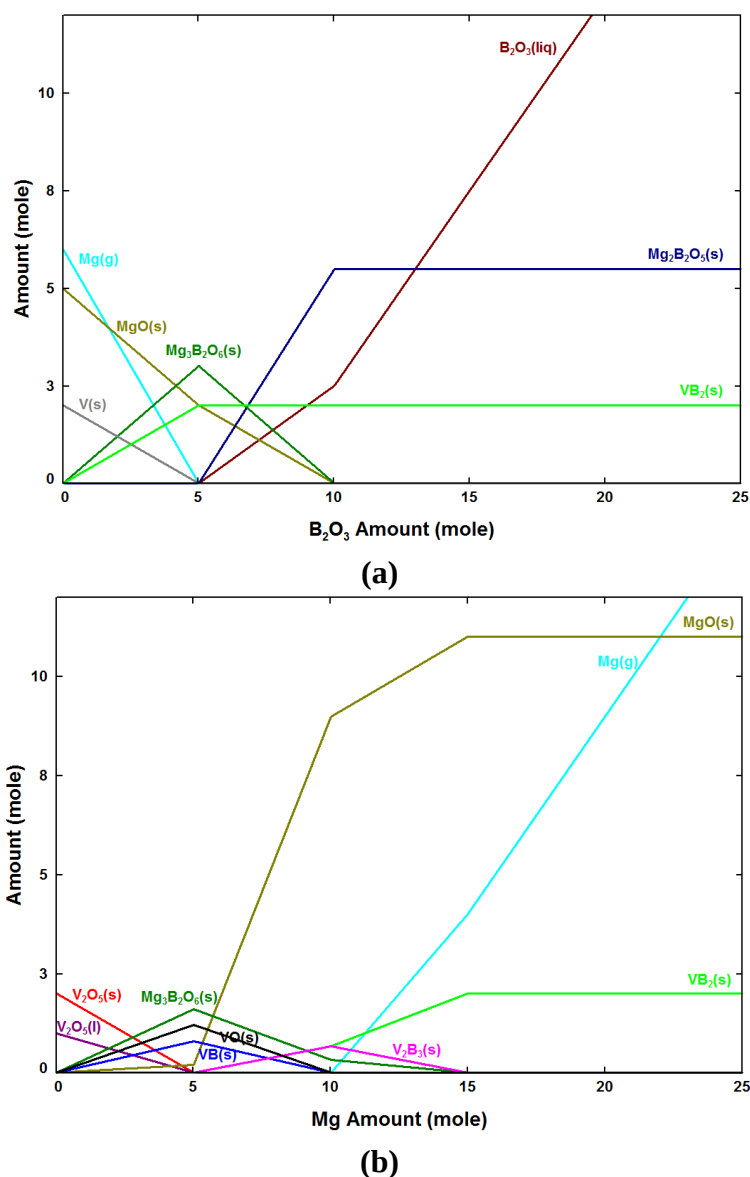


**Figure 3.8 :** Molar amounts of reactants/products of the reaction (3.1) at 1400°C varying according to the (a)  $B_2O_3$  amount and (b) Mg amount.

For the accurate prediction of the reaction mechanisms, FactSage<sup>TM</sup> thermodynamic calculations are compared to the phase detection and thermal analyses and explained in ‘Results and Discussion’ section in detail. The results of the thermodynamic calculations show only the equilibrium phase compositions without considering synthesis history and reaction kinetics. Due to the fact that milling processes are far from equilibrium, synthesized phases cannot be expected to have complete consistence with the thermodynamically calculated phases.



## 4. RESULTS AND DISCUSSION

This chapter of the dissertation includes four sections which explain and discuss about the experimental results of the solid-state synthesis of vanadium and niobium boride powders and the consolidation of them by the detailed characterization investigations. The first three sections explain the mechanochemical synthesis of vanadium and niobium boride powders and milling-assisted carbothermal production of the niobium boride-based composite powders. The ball milling parameters such as milling time and amount of the reactants are varied during the both synthesis methods. In the final section, consolidation and bulk properties of the vanadium and niobium borides are investigated. Microstructural and mechanical characterizations of the sintered vanadium and niobium boride products are reported and discussed regarding the effect of different production conditions and sintering methods on the bulk properties.

### 4.1 Mechanochemical Synthesis of the Vanadium Boride Powders

This section reveals the results of a detailed phase analyses on the milled and leached powders. These results are discussed in the sense of the proposed production route of the vanadium boride powders, which is reaction-induced mechanical milling followed by leaching and the stoichiometry of the initial powders used in. Moreover, microstructure and some properties of the powders are investigated by XRD, SM, SEM/EDX, TEM, DSC analyses and density and particle size measurements.

Figure 4.1 shows the XRD patterns of the as-blended  $V_2O_5$ - $B_2O_3$ -Mg powders and those milled for 0, 15 and 30 min. It is evident from Figure 4.1 that there is no reaction after milling 15 min since  $V_2O_5$  (ICDD Card No: 89-0611, Bravais lattice: primitive orthorhombic,  $a=1.154$  nm,  $b=0.438$  nm,  $c=0.357$  nm) and Mg (ICDD Card No: 35-0821, Bravais lattice: primitive hexagonal,  $a=b=0.329$  nm,  $c=0.521$  nm) phases are still present in the powder blend. No peaks belonging to the  $B_2O_3$  phase can be observed in the XRD patterns of the as-blended and 15 min of milled powders, which can be attributed to its amorphous nature. When as-blended and 15

min of milled powders are compared to each other, it is observed that the peak intensities of Mg considerably decreased after milling for 15 min which indicates a reduction in its crystallite size and means the reaction gets closer. After milling for 30 min,  $V_2O_5$  phase is completely disappeared and the  $VB_2$  (ICDD Card No: 38-1463, Bravais lattice: primitive hexagonal,  $a=b=0.299$  nm,  $c=0.306$  nm), VB (ICDD Card No: 30-1416, Bravais lattice: base-centred orthorhombic,  $a=0.306$  nm,  $b=0.805$  nm,  $c=0.297$  nm) and MgO (ICDD Card No: 01-079-0612, Bravais lattice: face-centred cubic,  $a=b=c=0.422$  nm) phases are formed with the presence of  $VO_x$  and unreacted Mg. This indicates that a solid-state reaction took place between the raw materials of  $V_2O_5$ ,  $B_2O_3$  and Mg resulting in the vanadium boride phases in two different compositions. The occurrence of the reaction (3.1) such a short milling time of 30 min can be attributed to its negative standard Gibbs free energy change of -2850 kJ at room temperature which makes the formation of  $VB_2$  easier. However, some amount of the  $V_2O_5$  phase reduced by Mg to vanadium suboxide phases ( $VO_x$ ). Additionally,  $VO_x$  and Mg phases are remained in the microstructure without taking place in a reaction.

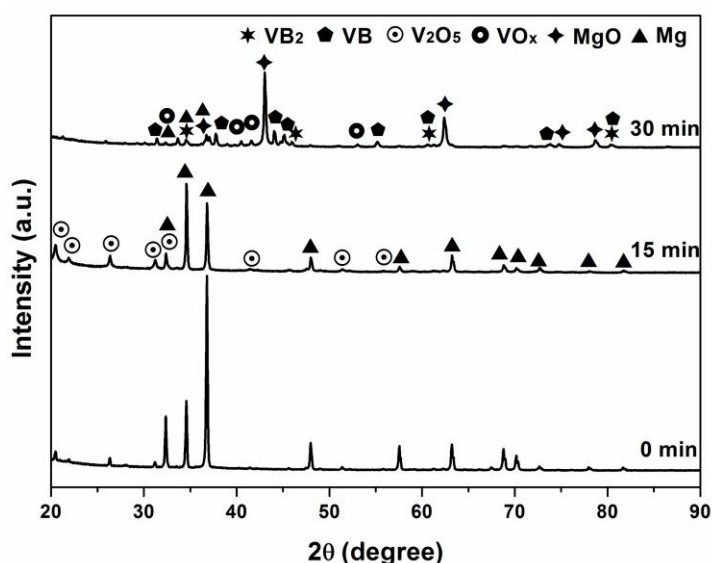


**Figure 4.1 :** XRD patterns of the as-blended  $V_2O_5$ - $B_2O_3$ -Mg powders and those milled for 0, 15 and 30 min.

Milling was extended up to 9 h in order to detect any probable degradation of the current reaction products and any formation of new phases. Figure 4.2 displays the XRD patterns of the  $V_2O_5$ - $B_2O_3$ -Mg powders milled for 1, 2, 3, 5, 7 and 9 h. As seen from Figure 4.2, there is no change in the XRD patterns of the milled powders indicating that extended milling has no effect on the mechanochemical reaction if

stoichiometric amounts of the starting materials are used. On the other hand, there are not any elemental V or B (reduced from their oxides) and additional compounds between V-Mg, B-Mg, V-Mg-O, V-B-O, B-Mg-O, etc. in the detection limit of XRD, even the milling time prolonged up to 9 h. The reason of the formation of  $\text{VO}_x$  and unreacted Mg may be insufficient amounts of the boron source or reducing agent. It is obvious that using stoichiometric amounts of the initial powders is not appropriate for the complete reduction and for the high-purity vanadium boride synthesis. Therefore, the stoichiometric excess amounts of them were also used during milling experiments in order to observe the possible change in their microstructures.

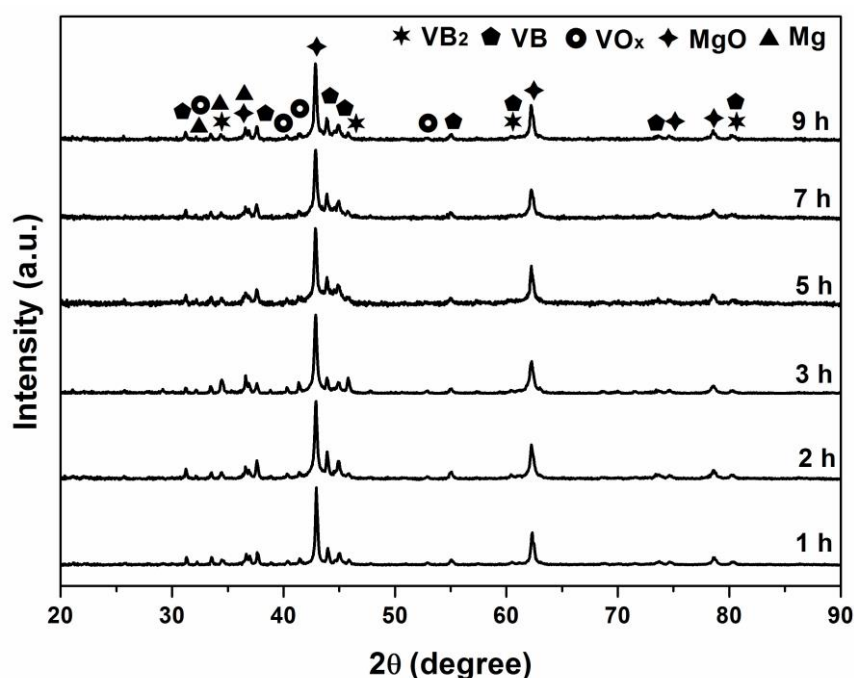


**Figure 4.2 :** XRD patterns of the  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for different times.

#### 4.1.1 The effect of excess $\text{B}_2\text{O}_3$ and Mg on the reaction products

Figure 4.3 presents the XRD patterns of the  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 5 h with 50 wt. % excess of  $\text{B}_2\text{O}_3$  before and after leaching with 4 M HCl. As seen from Figure 4.3(a), XRD pattern of the  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 5 h with 50 wt. % excess of  $\text{B}_2\text{O}_3$  exhibits the VB,  $\text{VB}_2$ ,  $\text{V}_3\text{B}_4$  (ICDD Card No: 09-0321, Bravais lattice: body-centred orthorhombic,  $a=0.303$  nm,  $b=1.318$  nm,  $c=0.299$  nm), MgO and  $\text{Mg}_3\text{B}_2\text{O}_6$  (ICDD Card No: 03-0823, Bravais lattice: primitive orthorhombic) phases. The utilization of stoichiometric excess amount of  $\text{B}_2\text{O}_3$  provides completing the reduction process and provides the disappearance of  $\text{VO}_x$  and unreacted Mg

phases. However, it is likely that some of the excess  $B_2O_3$  has reacted with  $MgO$  to form the  $Mg_3B_2O_6$  phase. This result also conforms well to the thermodynamic calculations given in Figure 3.8(a) where the formation of  $Mg_3B_2O_6$  phase was predicted. As seen in Figure 4.3(b), the peaks of VB as major phase and  $VB_2$ ,  $V_3B_4$  and  $Mg_3B_2O_6$  are identified after leaching of the powders.  $MgO$  phase observed in the milled powders is disappeared after leaching with 4 M HCl indicating a successful removal of the undesired phase, whereas  $Mg_3B_2O_6$  is still present in the structure. It is also seen in Figure 4.3(b) that some of the peaks of  $Mg_3B_2O_6$  phase disappeared due to the partial dissolution in excess amount of HCl (4 M) during leaching. It is essential to prevent the formation of magnesium borate phases during milling since they cannot be completely removed by leaching treatments in HCl solution. Increasing the milling time was not considered as an appropriate solution for this problem since the amounts of phases did not change with extended milling times (Figure 4.2). It was also expected that higher mechanical milling times may trigger the reactions occurring between the excess amount of  $B_2O_3$  and  $MgO$ . Therefore, the stoichiometric excess amounts of reducing agent were used in the following experiments in order to observe the possible change in the microstructures of the powders.

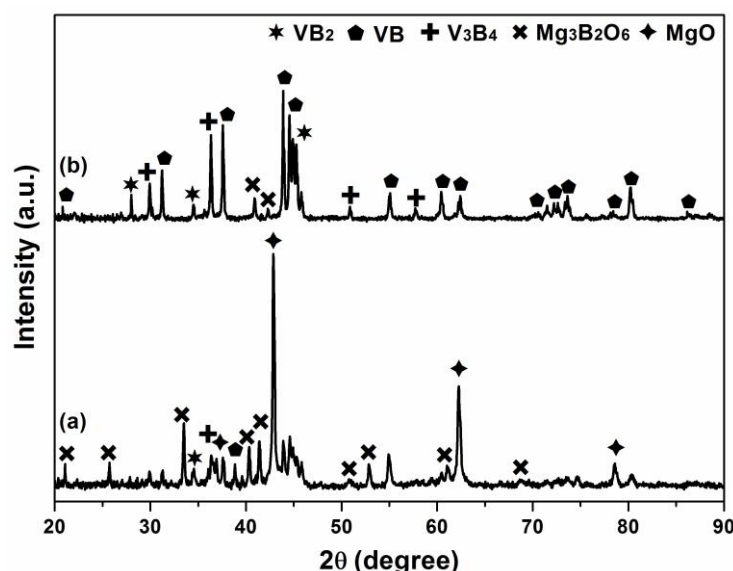


**Figure 4.3 :** XRD patterns of the  $V_2O_5$ - $B_2O_3$ -Mg powders milled for 5 h with 50 wt. % excess of  $B_2O_3$  (a) before leaching and (b) after leaching with 4 M HCl.

Figure 4.4 shows the XRD patterns of the  $V_2O_5$ - $B_2O_3$ -Mg powders milled for different times with 25 or 50 wt. % excess of Mg. As seen from Figure 4.4(a)-(d), all

XRD patterns exhibit the  $\text{VB}_2$ , VB and MgO phases, indicating that the formations of  $\text{VO}_x$  and magnesium borate phases and the presence of unreacted Mg were prevented when Mg was used in excess amounts. The elimination of the formation of vanadium oxide and magnesium borate phases during the use of 50 % stoichiometric excess of Mg was also predicted by the thermodynamical calculations given in Figure 3.8(b). As also seen in Figure 4.4, milling for 5 or 7 h does not cause a significant change in the XRD patterns, whereas increasing Mg content affects the peak intensities. As the excess amount of Mg increases from 25 to 50 %, the amount of MgO increases and the amount of VB decreases (Figure 4.4(c)-(d)). Therefore, subsequent leaching treatment was carried out on the  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 7 h with 50 wt. % excess of Mg.

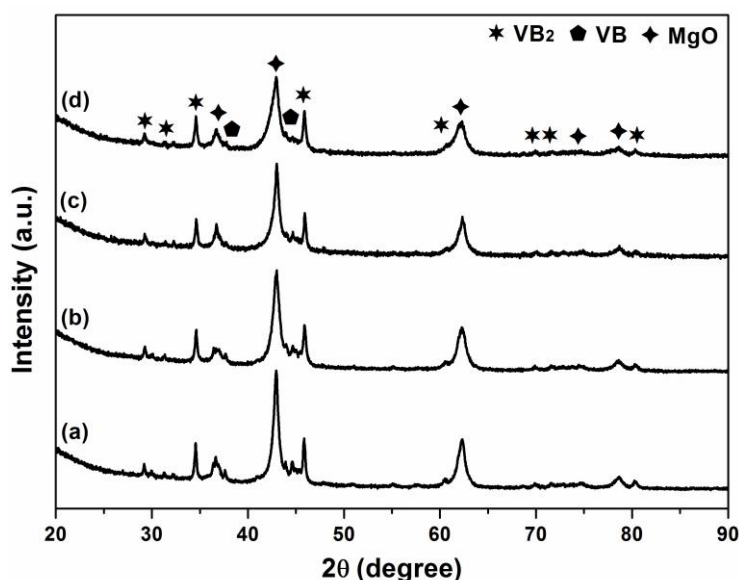


**Figure 4.4 :** XRD patterns of the  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders (a) milled for 5 h with 25 wt. % excess of Mg, (b) milled for 7 h with 25 wt. % excess of Mg, (c) milled for 5 h with 50 wt. % excess of Mg and (d) milled for 7 h with 50 wt. % excess of Mg.

Figure 4.5 shows the XRD patterns of the  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 7 h with 50 wt. % excess of Mg after leaching with 4 M HCl. Figure 4.5 reveals that the unwanted by-product MgO was completely removed from the powder blend after leaching with 4 M HCl and pure vanadium boride powders comprising  $\text{VB}_2$ , VB and  $\text{V}_3\text{B}_4$  phases were obtained. The observation of  $\text{V}_3\text{B}_4$  phase after leaching could be explained with its small amount dominated by higher peak intensities of other present phases, especially MgO. As seen from the XRD patterns of the leached samples, there is no residual Mg chloride, oxychloride or hydroxychloride as

leaching products which indicates the effectiveness of the leaching parameters. AAS analysis of the leach solution showed that the Mg and Fe amounts in the composition of the leach solution are 5230 and 56 ppm, respectively. Thus, the dissolution of MgO was also confirmed by AAS analyses of the leach solutions decanted from the residual powders. Furthermore, Fe impurity released from the milling media was removed by HCl leaching as well as MgO.  $\text{VB}_2$  is the dominant phase in the microstructure in consistent with the ideal reaction (3.1) and as expected from thermodynamical calculations given in Figure 3.8(b). However, unlike the ideal condition and thermodynamical predictions, small amounts of VB and  $\text{V}_3\text{B}_4$  phases are also formed even if 50 % excess amount of Mg reducing agent is used. It has been already reported that single-phase vanadium boride could not be obtained via arc melting or direct solid-state reaction of elemental powders at high temperatures even though specific ratios of elemental V and B were used as the initial compositions according to the V-B binary phase diagram (Nunes et al, 2004; Okada et al, 2008). This can be attributed to the proposed V-B binary phase diagrams in the literature (Figure 2.1), in which  $\text{VB}_2$  ( $T_m \sim 2750^\circ\text{C}$ , 67 at. % B), VB ( $T_m \sim 2570^\circ\text{C}$ , 50 at. % B) and  $\text{V}_3\text{B}_4$  ( $T_m \sim 2640^\circ\text{C}$ , 57 at. % B) phases were defined as stable compounds having very close melting points and homogeneity ranges. It is also understandable that products of the actual reaction triggered by the mechanical milling which is away from the equilibrium conditions may not completely conform to those of the ideal one. On the other hand, single phase  $\text{VB}_2$  nanopowders could be achieved by mechanochemical reaction of  $\text{VCl}_3$ ,  $\text{LiBH}_4$  and  $\text{LiH}$  according to the reaction (2.8) and subsequent leaching (Kim et al, 2008). As the Gibbs free energy changes of the reactions (2.8) and (3.1) compare to each other,  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  system has much more negative Gibbs free energy change (-2850 kJ) than that of  $\text{VCl}_3\text{-LiBH}_4\text{-LiH}$  system (-523 kJ) at room temperature. Kim et al (2008) also reported that LiCl was added to the raw materials in order to keep the temperature as low as possible during mechanochemical processing. Thus, preventing the large amount of heat released during milling and providing a relative decrease in temperature may be the reason of the formation of single phase  $\text{VB}_2$  instead of the formation of multi-phases. Large amount of heat released during milling is corresponding to intensive exothermic reactions in which ignited particles interact with each other in their every single point. This phenomenon increases the possibility of yielding products in different stoichiometries.

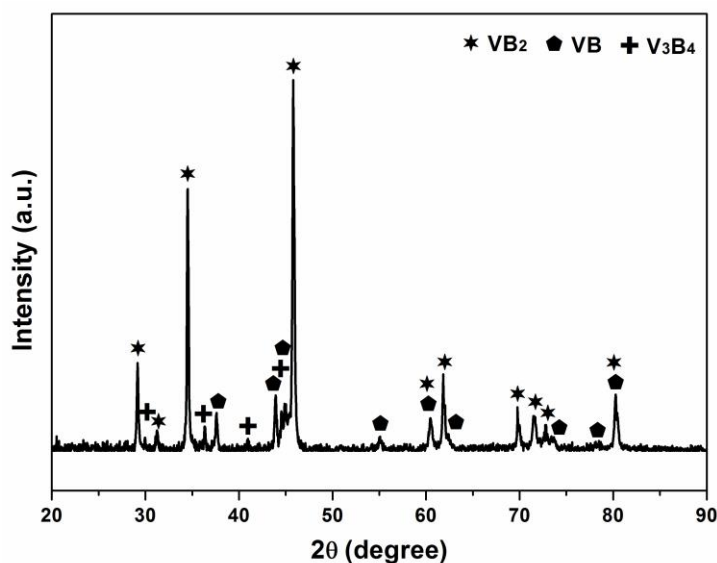


**Figure 4.5 :** XRD pattern of the  $V_2O_5$ - $B_2O_3$ -Mg powders milled for 7 h with 50 wt. % excess of Mg after leaching with 4 M HCl.

Although thermodynamical calculations given in Figure 3.8(b) exhibited the maximum value of  $VB_2$  formation at 50 % excess Mg amount, 75 wt. % excess amount of Mg was also examined in the milling experiments to reveal the possible changes occurring due to the kinetic factors. Figure 4.6 shows the XRD patterns of the  $V_2O_5$ - $B_2O_3$ -Mg powders milled for 7 h with 75 wt. % excess of Mg before and after leaching with 4 M HCl. Figure 4.6(a) shows the XRD peaks of  $VB_2$ , VB and MgO phases with the presence of an undefined phase at  $2\theta=32$ , 48 and  $58^\circ$ . After HCl leaching (Figure 4.6(b)), the undefined phase and MgO were completely removed from the powders and  $VB_2$ , VB and  $V_3B_4$  phases were obtained. The formation of the undefined phase is believed to be associated with the reaction between the starting powders and free Fe resulting from the wear contamination of the milling media. It is also known that this undefined phase can not be an iron boride whose compounds are not soluble in HCl. It is probably a Fe-Mg alloy which can form spontaneously due to the high amount of ductile Mg in the powders. The ductility of Mg can facilitate its welding on worn Fe. Considering both Mg and Fe are soluble in HCl, the undesired phase can be a Fe-Mg alloy with high possibility. The AAS analysis of the leach solution also supports this idea since the amount of Fe is detected as 610 ppm in the leach solution which is considerably high. Furthermore, as expected, the amount of Mg in the leach solution is measured as 6560 ppm which is higher than that of the  $V_2O_5$ - $B_2O_3$ -Mg powders milled for 7 h with 50 wt. % excess of Mg. Thus, the high amount of MgO and the undesired phase in the milled

powders, which are dissolved during HCl leaching, result in high Fe and Mg contents in the leach solution of the  $V_2O_5$ - $B_2O_3$ -Mg powders milled for 7 h with 75 wt. % excess of Mg. Although the  $V_2O_5$ - $B_2O_3$ -Mg powders containing 50 and 75 wt. % excess of Mg were milled at the same time of 7 h, much more Fe contamination from the milling media and hence the formation of undesired phase occurred in the case of using 75 % excess of Mg. This can be due to the decreased ratio of  $B_2O_3$  which also acts as a process control agent or behaves as a wax during milling and prevents the adherence of the powders to the milling media. When Mg is used in 75 % excess amount, the lubricating effect of  $B_2O_3$  decreases and the Fe contamination from milling media increases. As Figure 4.5 and 4.6(b) compare to each other, it is evident that the utilization of 75 % stoichiometric excess amount of Mg provides a considerable decrease in the amount of VB and  $V_3B_4$  phases in the total powder blend and getting closer to the single phase  $VB_2$  from multi phases. However, the total powder amount extracted after milling for 7 h of  $V_2O_5$ - $B_2O_3$ -Mg powders with 75 wt. % excess of Mg is lower than that of powders milled with 50 wt. % excess of Mg. This is due to the adherence of the powders on the inner walls of the vial which also means a decrease in the molar yield of  $VB_2$  synthesis in the powders containing 75 % excess of Mg. Thus, the optimum Mg content can be determined as 50 wt. % stoichiometric excess amount of Mg in the total powder blend to synthesize vanadium boride powders.

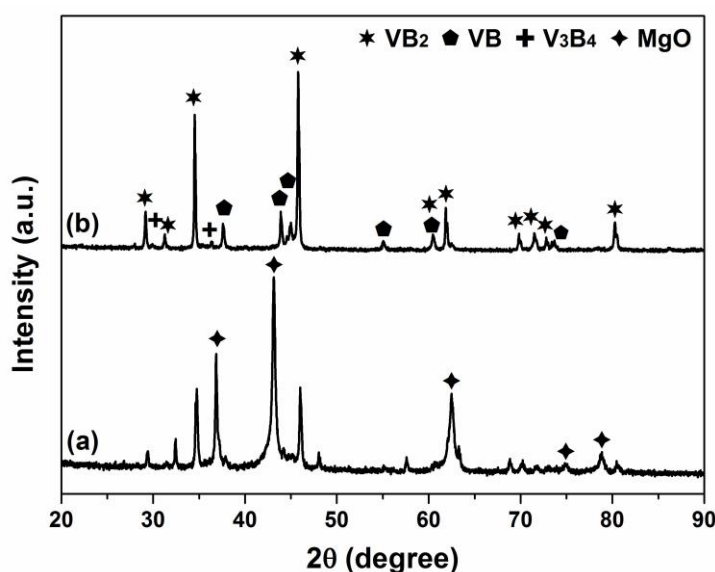


**Figure 4.6 :** XRD patterns of the  $V_2O_5$ - $B_2O_3$ -Mg powders milled for 7 h with 75 wt. % excess of Mg (a) before leaching and (b) after leaching with 4 M HCl.

In order to determine the thermal behaviour of the powders prepared in optimum conditions, DSC analysis was conducted on the  $V_2O_5$ - $B_2O_3$ -Mg powders milled for 7 h with 50 wt. % excess of Mg after leaching with 4 M HCl (Figure 4.7). DSC analysis is a good verification of the formation of new phases since it should reveal different thermal behaviours when different phases are present in the structure. The small amounts of the phases can be determined even if they cannot be detected by XRD. As seen from Figure 4.7, DSC scan of the milled and leached powders do not show any exothermic or endothermic peaks. There is only a decreasing tendency in heat flow values at temperatures higher than 1000°C which can be associated with the phase transformations of the vanadium borides at higher temperatures. Apart from that, the formation of new phases occurring due to the reactions between the components or the melting of a remained phase should reveal whether small or sharp peaks. Thus, the absence of any endothermic or exothermic peaks in the DSC scan of the powders given in Figure 4.7 is the solid evidence of sufficient purity that milled powders achieved after leaching with 4 M HCl. On the basis of XRD, AAS, DSC analyses of the milled powders after leaching treatment, it is clear that the resultant powders do not include any contamination or other unwanted reaction products.

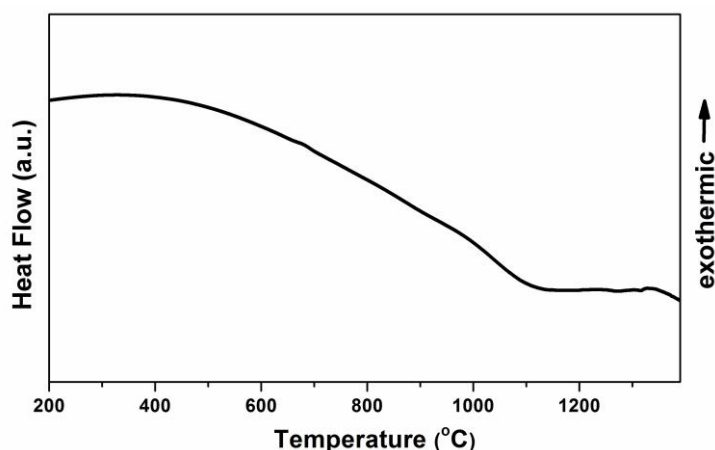


**Figure 4.7 :** DSC scan of the  $V_2O_5$ - $B_2O_3$ -Mg powders milled for 7 h with 50 wt. % excess of Mg after HCl leaching.

#### 4.1.2 Microstructure and properties of the powders

Before the characterization studies of the powders, phase analyses and density measurements of the commercial powders were also carried out in order to compare the commercial and the laboratory synthesized powders. Figure 4.8 shows the XRD patterns of commercial VB (Alfa Aesar<sup>TM</sup> 42212) and  $VB_2$  (ABCR<sup>TM</sup> 102696)

powders. The XRD pattern of the commercial VB powders reveals the VO<sub>2</sub> peaks with the presence of small amount of VB<sub>2</sub> phase, whereas the commercial VB<sub>2</sub> powders includes considerable amount of VO<sub>2</sub>.

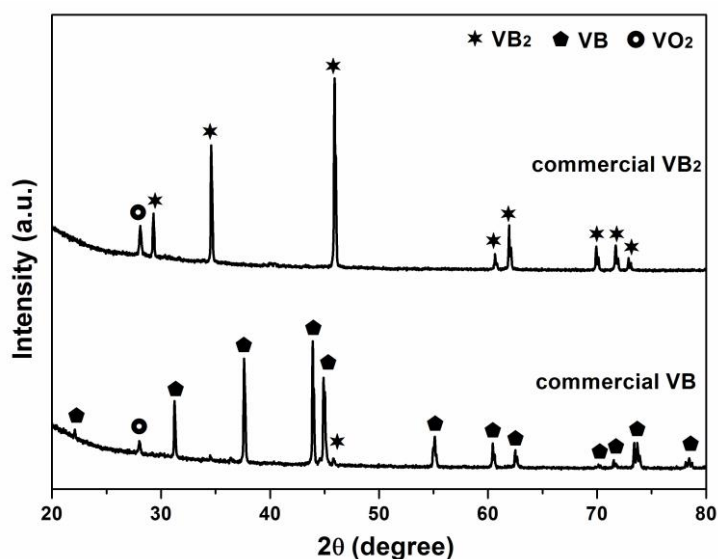


**Figure 4.8 :** XRD patterns of the commercial VB<sub>2</sub> and VB powders.

Average density values of the laboratory-synthesized (originated from the mechanochemical synthesis of V<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-Mg blends) and commercial vanadium boride powders are given in Table 4.1. The theoretical densities of VB<sub>2</sub>, VB and V<sub>3</sub>B<sub>4</sub> are 5.01, 5.63 and 5.46 g/cm<sup>3</sup>, respectively. The average density values of the commercial VB<sub>2</sub> and VB powders are respectively 3.33 and 3.82 g/cm<sup>3</sup>, which are much lower than those of the theoretical ones. This is due to the presence of VO<sub>2</sub> phase confirmed by XRD patterns given in Figure 4.8 and other possible impurities having low density values which cannot be detected by XRD analysis. On the other hand, laboratory-synthesized VB<sub>2</sub>-dominant and VB-dominant powders respectively have the average density values of 4.96 and 4.34 g/cm<sup>3</sup>, which are higher than those of the commercial ones. The relatively lower density value of the VB-V<sub>3</sub>B<sub>4</sub>-VB<sub>2</sub> powders (d=4.34 g/cm<sup>3</sup>) than that of the VB<sub>2</sub>-VB-V<sub>3</sub>B<sub>4</sub> (d=4.96 g/cm<sup>3</sup>) can be associated with the Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub> phase (d=3.04 g/cm<sup>3</sup>) existing in the structure of the powders milled with 50 wt. % excess of B<sub>2</sub>O<sub>3</sub> (Figure 4.3(b)). The average density value of 4.96 g/cm<sup>3</sup> was achieved for the V<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-Mg powders milled for 7 h with 50 wt. % excess of Mg, which is very close to the theoretical density of VB<sub>2</sub>.

**Table 4.1 :** Average density values of the mechanochemically-synthesized powders from  $V_2O_5$ - $B_2O_3$ -Mg blends and commercial vanadium boride powders.

| Sample                                                                                                                                                                                                                   | Average Density ( $g/cm^3$ ) |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|
| VB <sub>2</sub> -VB-V <sub>3</sub> B <sub>4</sub> prepared by milling for 7 h with 50 wt. % excess of Mg after HCl leaching<br>(without impurity)                                                                        | $4.96 \pm 0.015$             |
| VB- V <sub>3</sub> B <sub>4</sub> -VB <sub>2</sub> prepared by milling for 5 h with 50 wt. % excess of B <sub>2</sub> O <sub>3</sub> after HCl leaching<br>(with Mg <sub>3</sub> B <sub>2</sub> O <sub>6</sub> impurity) | $4.34 \pm 0.010$             |
| Commercial VB <sub>2</sub> (with VO <sub>2</sub> impurity)                                                                                                                                                               | $3.33 \pm 0.006$             |
| Commercial VB-VB <sub>2</sub> (with VO <sub>2</sub> impurity)                                                                                                                                                            | $3.82 \pm 0.005$             |

Figure 4.9(a)-(f) show the SM images of the as blended  $V_2O_5$ - $B_2O_3$ -Mg powders and those milled and leached powders. As Figure 4.9(a) and (b) are compared to each other, the difference between the as-blended and milled powders can be clearly seen: As-blended powders contain the mixtures of  $V_2O_5$ ,  $B_2O_3$  and Mg particles in granular form, whereas 7 h of milled powders consist of agglomerated VB<sub>2</sub>, VB, VO<sub>x</sub>, MgO and Mg particles according to their XRD patterns (Figure 4.1 and 4.2). This morphological difference has expected after milling since fresh surfaces of the particles have tendencies to agglomerate with each other. This phenomenon can also be seen in Figure 4.9(c) and (e) which show the SM images of the powders milled with 50 wt. % excess amounts of  $B_2O_3$  and Mg, respectively. Since these powders do not contain VO<sub>x</sub> and unreacted Mg particles according to their XRD patterns given in Figure 4.3(a) and 4.4(d), the colours differ from the powders milled for 7 h with stoichiometric amounts of the starting particles. As seen from Figure 4.9(c), the SM image of the powders milled for 5 h with 50 wt. % excess of  $B_2O_3$  have white regions containing Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub> phase (Figure 4.3(a)). After leaching with 4 M HCl (Figure 4.9(d)), the colours of the powders become relatively darker because of the complete dissolution of MgO and partial dissolution of some amount of Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub> (Figure 4.3(b)). On the other hand, SM image of the powders milled for 7 h with 50 wt. % excess of Mg after HCl leaching promotes the complete purification of the vanadium boride powders without any contamination, as considered along with its XRD pattern given in Figure 4.5.

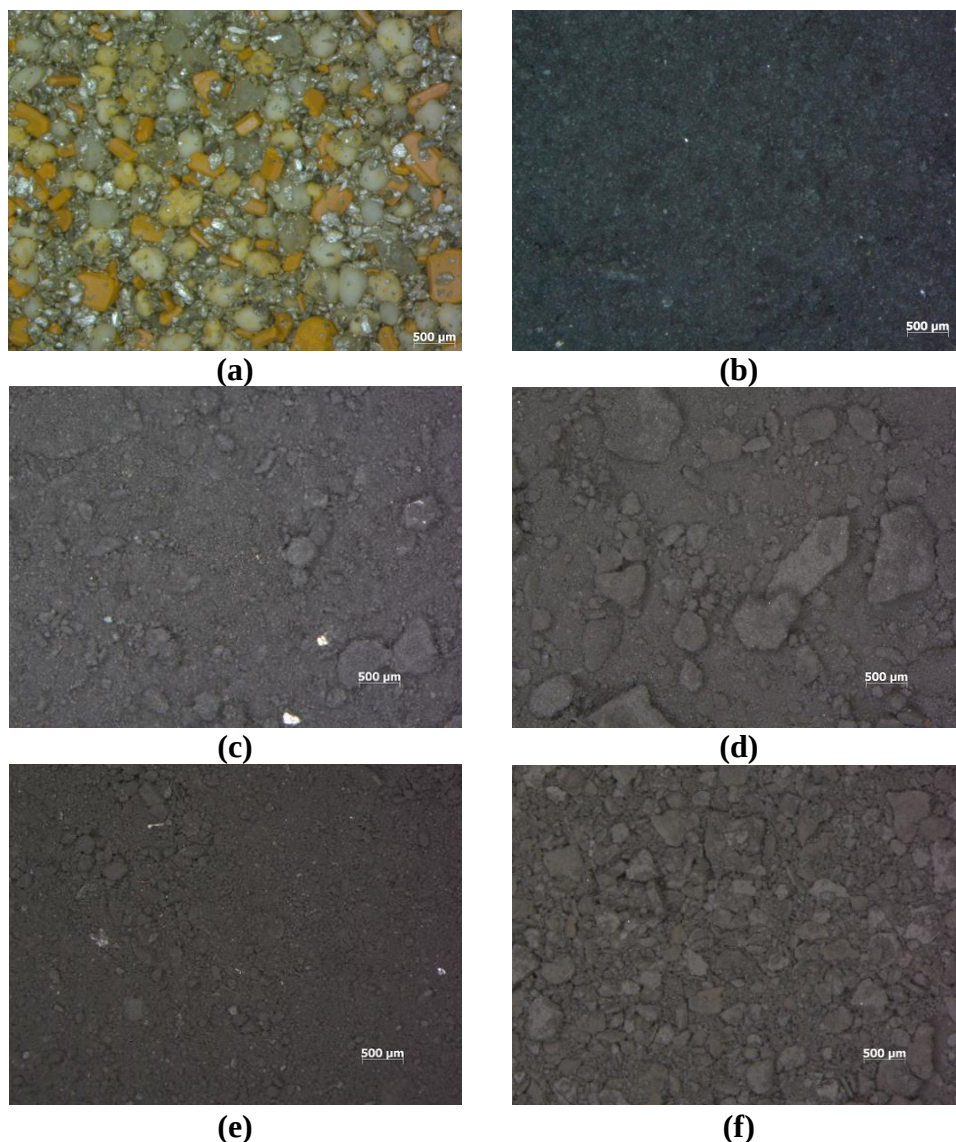


**Figure 4.9 :** SM images of the as blended  $V_2O_5$ - $B_2O_3$ -Mg powders and those milled and leached powders: (a) as-blended powders, (b) powders milled for 7 h, (c) powders milled for 5 h with 50 wt. % excess of  $B_2O_3$ , (d) powders milled for 5 h with 50 wt. % excess of  $B_2O_3$  after HCl leaching, (e) powders milled for 7 h with 50 wt. % excess of Mg and (f) powders milled for 7 h with 50 wt. % excess of Mg after HCl leaching.

Figure 4.10(a)-(c) show the secondary electron SEM images of the as-blended  $V_2O_5$ - $B_2O_3$ -Mg powders and those milled for 30 min and 7 h. As seen from Figure 4.10(a), as-blended powders contain irregular particles. Figure 4.10(b) clearly shows the adherence and agglomeration of the particles due to the heat released by the mechanochemical reaction, after milling for 30 min. The microstructure of the powders milled for 30 min (Figure 4.10(b)) involves round-shaped vanadium boride particles (Figure 4.1) embedded in irregular and large MgO particles with sizes of 1  $\mu m$  to 4  $\mu m$ . Plastic deformation, flattening and cold welding of Mg powders occur

in the early stage of ball milling which makes lamellar structures (Torabi et al, 2015). As the milling time extended to 7 h (Figure 4.10(c)), it is clearly seen that the particle sizes decrease below  $1.5\ \mu\text{m}$  due to the continuous fragmentation of the formed brittle components (vanadium borides and MgO) during milling. Higher magnification SEM image (80000X) in Figure 4.10(c) reveals clearer the agglomerated structure of the 7 h of milled powders where particles embedded in the agglomerates are smaller than 500 nm. In order to eliminate the agglomeration of the particles, powders were dispersed in distilled water by using a homogenizer prior to particle size measurements. Therefore, particle size measurement of the powders milled for 7 h presented in Figure 4.10(d) gives more accurate results as an average size about 279 nm.

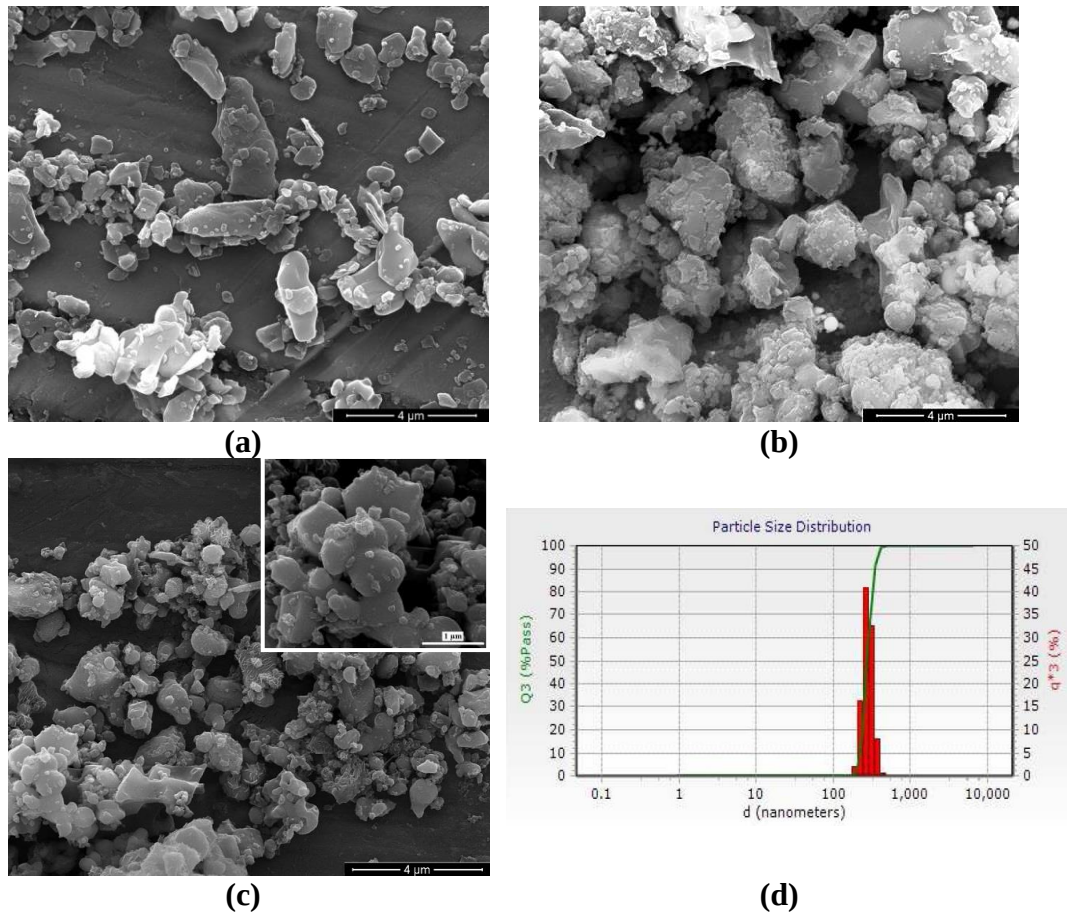


**Figure 4.10 :** SEM images of the as-blended  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders (a) and those milled for 30 min (b), for 7 h (c) and PSA image of the powders milled for 7 h (d).

Figure 4.11(a)-(d) show the SEM, TEM and PSA images of the  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 7 h with 50 wt. % excess of Mg after HCl leaching. Particles consisting of  $\text{VB}_2$ , VB and  $\text{V}_3\text{B}_4$  phases (Figure 4.5) can be seen in the SEM and

TEM images given in Figure 4.11(a)-(c): During the HCl leaching of MgO, the agglomerates were broken down and particles were liberated (Figure 4.11(a)). After the removal of MgO, the particle size was seen to be below 400 nm, as shown in Figure 4.11(b)-(c). The particle size measurement of the powders exhibits the average particle size of 171 nm (Figure 4.11(d)). The similar phenomenon was observed in the previous studies relating the mechanochemical synthesis of tungsten and molybdenum borides where the removal of MgO after HCl leaching has provided a significant decrease in the particle sizes of the final powders (Çamurlu, 2011; Coşkun and Öveçoğlu, 2013).

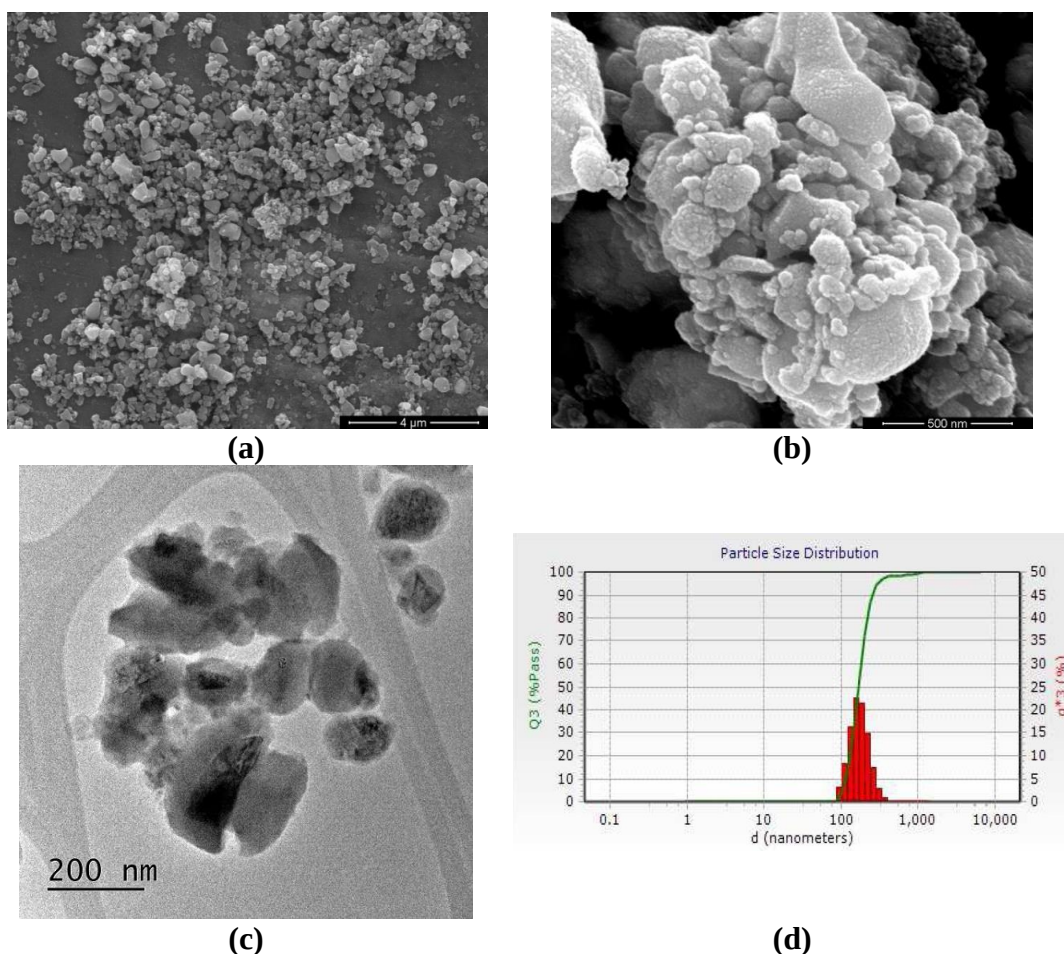


**Figure 4.11** : SEM, TEM and PSA images of the  $V_2O_5$ - $B_2O_3$ -Mg powders milled for 7 h with 50 wt. % excess of Mg after HCl leaching: (a) SEM image 20000X, (b) SEM image 160000X, (c) TEM image and (d) particle size measurement.

In order to reveal the phase distribution clearly, SEM/EDX analyses were carried out on compacted pellets. Figures 4.12(a)-(e) present the secondary electron SEM image and associated elemental maps for V, B, Mg and O taken from the pellet of the powders milled for 7 h with 50 wt. % excess of Mg. Figure 4.12(b) reveals some V-

rich regions which are due to the non-stoichiometric vanadium boride phases existing in the microstructure of the powders (Figure 4.4). The weak signals of B particles shown in Figure 4.12(c) can be associated with the suppression effect of the other strong signals of the elements (V, Mg and O). The elemental Mg map (Figure 4.12(d)) coincides almost entirely with the elemental O map (Figure 4.12(e)), suggesting the presence of the MgO phase. SEM/EDX analyses of the  $V_2O_5$ - $B_2O_3$ -Mg powders milled for 7 h with 50 wt. % excess of Mg confirms the phase analyses obtained by XRD (Figure 4.4). Furthermore, the distribution of the V, B, Mg and O elements throughout the microstructure reveals the adherence and simultaneous existence of vanadium boride and MgO phases.

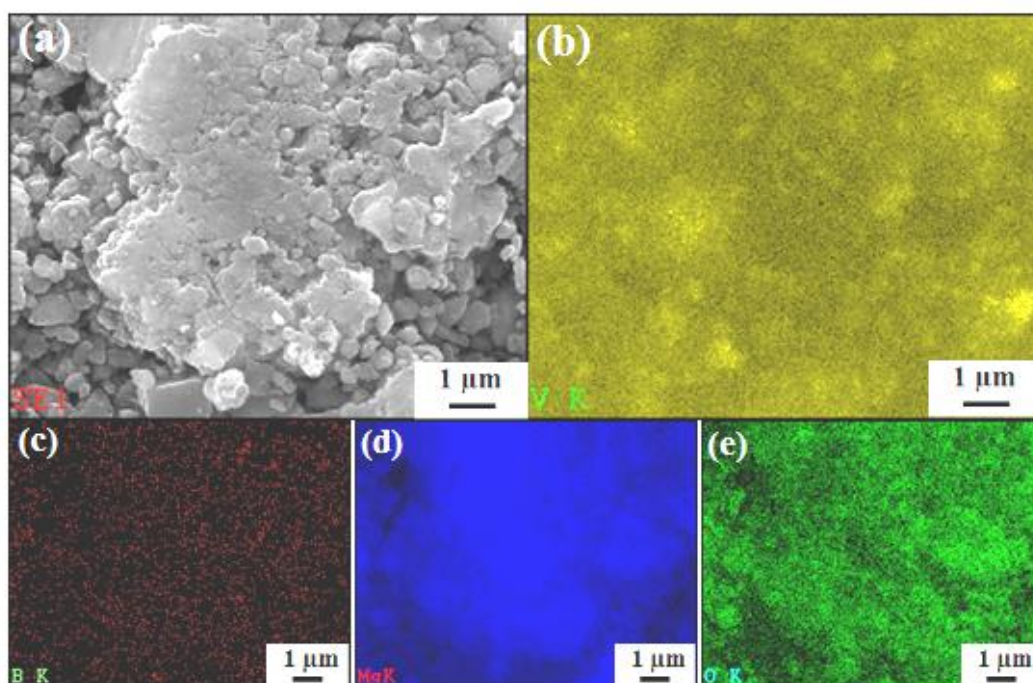


**Figure 4.12 :** SEM/EDX analyses of the pellet obtained from the compaction of the  $V_2O_5$ - $B_2O_3$ -Mg powders milled for 7 h with 50 wt. % excess of Mg: (a) SEM image of the pellet and corresponding elemental maps for (b) V, (c) B, (d) Mg and (e) O.

Figure 4.13 shows the SEM/EDX analyses of the pellet obtained from the compaction of the  $V_2O_5$ - $B_2O_3$ -Mg powders milled for 7 h with 50 wt. % excess of Mg after 4 M HCl leaching. The EDS spectra taken from different regions shown in the SEM image of the powders (Figure 4.13(a)) did not reveal any presence of MgO phase. It reveals that  $2.56 \pm 0.35$  wt. % O was present in the microstructure which is due to the surface oxidation of the powders handling in laboratory atmosphere. This reflects on the EDX analysis of the powders as very weak O signals which shown in

Figure 4.13(d). On the other hand, the elemental V map (Figure 4.13(b)) coincides almost entirely with the elemental B map (Figure 4.13(c)), suggesting the presence of vanadium boride phases. Furthermore, as Figure 4.12(b)-(c) and Figure 4.13(b)-(c) compare to each other, it is clear that the signals arising from V and B elements considerably increased after leaching treatment. Besides, any signals of Mg or other elements (Fe, Ni etc.) were not detected during SEM/EDX analyses of the leached powders. This is the result of the entirely removal of unwanted MgO phase (Figure 4.5) and other possible impurities from the milled powders after HCl leaching which also proves the purity of the resultant vanadium boride powders.

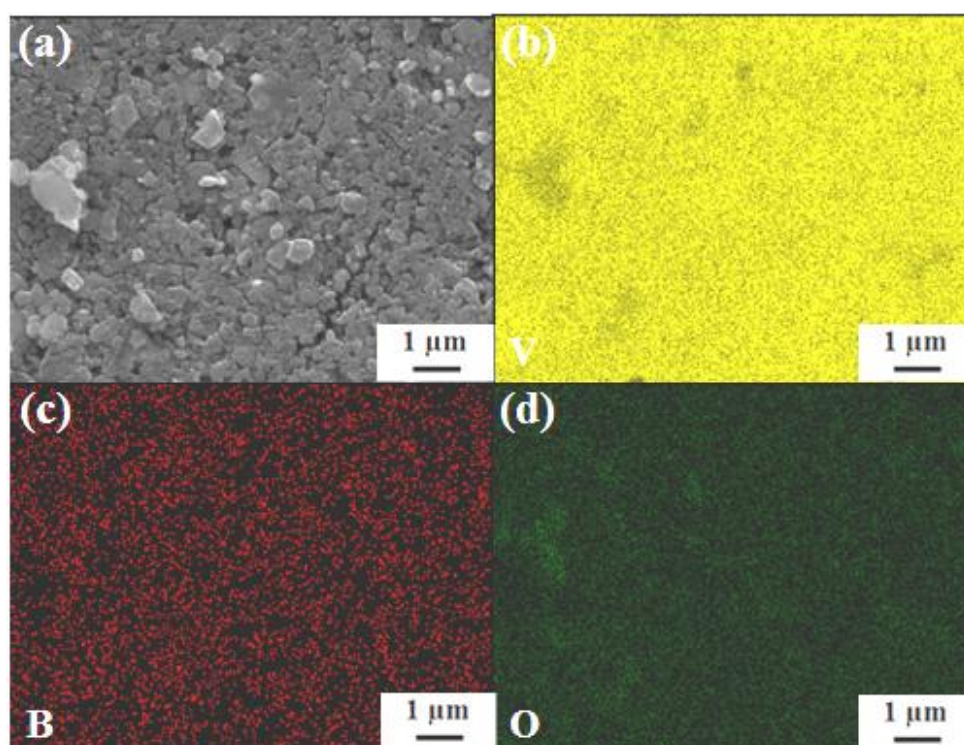


**Figure 4.13 :** SEM/EDX analyses of the pellet obtained from the compaction of the  $V_2O_5$ - $B_2O_3$ -Mg powders milled for 7 h with 50 wt. % excess of Mg after HCl leaching: (a) SEM image of the pellet and corresponding elemental maps for (b) V, (c) B and (d) O.

Figure 4.14(a)-(c) show the TEM investigations for the  $V_2O_5$ - $B_2O_3$ -Mg powders milled with 50 wt. % excess of Mg after 4 M HCl leaching. Figure 4.14(a) is a bright-field (BF) image of spheroidal particles and Figure 4.14(b) is the selected area diffraction pattern (SADP) taken from this particle (The camera length is 120 cm and zone axis is  $[0\bar{1}0]$ ). SADP reveals the presence of the hexagonal  $VB_2$  phase which was also detected as the dominant phase in the XRD pattern given in Figure 4.5. A high-resolution TEM (HRTEM) image taken from the particle in Figure 4.14(a) is

given in Figure 4.14(c). The lattice spacing of 0.198 nm can be indexed which corresponds to the (101) plane. The strongest peak in the XRD pattern of these powders given in Figure 4.5 corresponds to the (101) plane for the hexagonal  $\text{VB}_2$  phase. Additional TEM characterizations carried out on other regions of the same particle shown in Figure 4.14(a) revealed the spot patterns of single crystalline particles with different zone axes, all belonging to the  $\text{VB}_2$  phase.

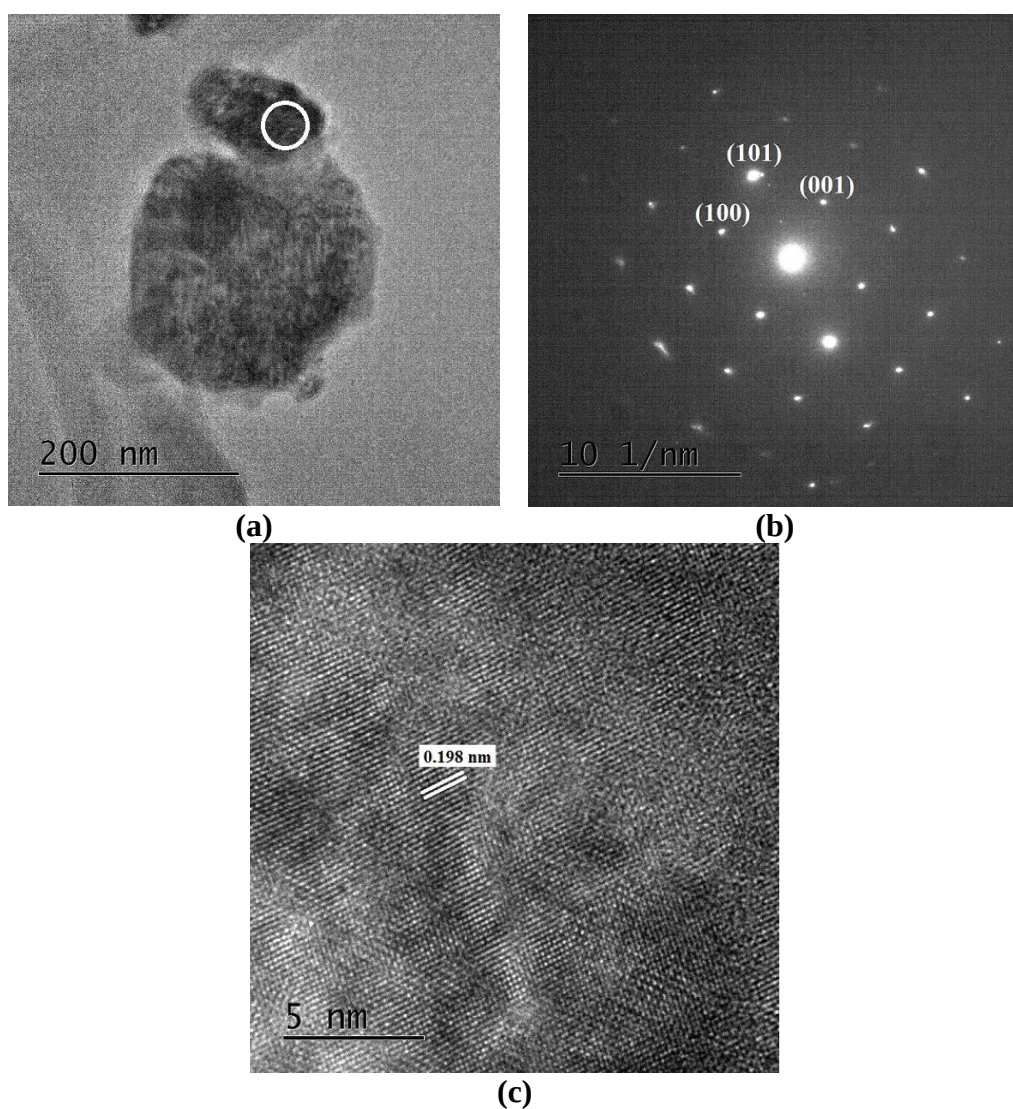


**Figure 4.14 :** TEM images of the  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 7 h with 50 wt. % excess of Mg after HCl leaching (a) bright-field (BF) image, (b) its corresponding selected area diffraction pattern (SADP) revealing the presence of the  $\text{VB}_2$  phase (The camera length is 120 cm and zone axis is  $[0\bar{1}0]$ ) and (c) HRTEM image.

Figure 4.15(a)-(b) show the BF image of an another particle from the same powders and its SADP taken from this particle (The camera length is 120 cm and zone axis is  $[\bar{3}10]$ ). SADP given in Figure 4.14(b) reveals the presence of the single-crystalline

orthorhombic VB phase which was also detected as a secondary phase in the XRD pattern given in Figure 4.5. Furthermore, BF images given in Figure 4.14(a) and 4.15(a) consist of particles with sizes of 100 to 400 nm, which conform well to the SEM analyses and particle size measurements (Figure 4.11).

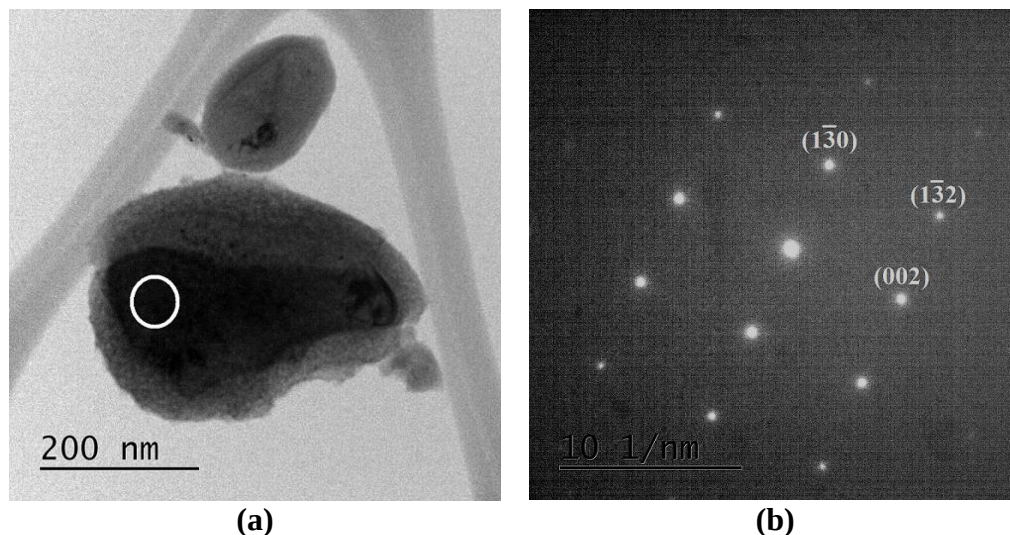


**Figure 4.15 :** TEM image of the  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 7 h with 50 wt. % excess of Mg after HCl leaching (a) bright-field (BF) image and (b) its corresponding selected area diffraction pattern (SADP) revealing the presence of the VB phase (The camera length is 120 cm and zone axis is  $[\bar{3}10]$ ).

As a conclusion,  $\text{VB}_2\text{-VB-V}_3\text{B}_4$  powders with an average particle size of 171 nm were obtained in high purity without any intermediate phase and any impurity via mechanochemistry by mechanical milling of the  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders for 7 h with 50 wt. % stoichiometric excess of Mg and subsequent leaching with 4 M HCl. Thus, a novel and simple solid-state synthesis method was achieved to fabricate nano-sized vanadium boride powders in high-purity through an economical way from their oxide raw materials in the presence of a strong reducing agent.

## 4.2 Mechanochemical Synthesis of the Niobium Boride Powders

In this section, the utilization of  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders for the mechanochemical synthesis of niobium boride powders are examined with the help of XRD, SEM/EDX, SM, TEM, DSC and AAS analyses and particle size, surface area and magnetic measurements.

Figure 4.16 presents the XRD patterns of the as-blended  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders and those milled for different times. It is evident from Figure 4.16 that there is no

reaction after milling for 1 h since Nb<sub>2</sub>O<sub>5</sub> (ICDD Card No: 01-071-0336, Bravais lattice: primitive orthorhombic, a=0.617 nm, b=2.917 nm, c=0.393 nm) and Mg (ICDD Card No: 35-0821, Bravais lattice: primitive hexagonal, a=b=0.329 nm, c=0.521 nm) phases are still present in the powder blend. No peaks belonging to the B<sub>2</sub>O<sub>3</sub> phase can be observed in the XRD patterns of the as-blended and 1 h of milled powders, which can be attributed to its amorphous nature. After milling for 2 h, the NbB (ICDD Card No: 32-0709, Bravais lattice: base-centered orthorhombic, a=0.330 nm, b=0.872 nm, c=0.317 nm), NbB<sub>2</sub> (ICDD Card No: 35-0742, Bravais lattice: primitive hexagonal, a=b=0.311 nm, c=0.327 nm), Nb<sub>3</sub>B<sub>4</sub> (ICDD Card No: 03-065-2553, Bravais lattice: body-centred orthorhombic, a=0.330 nm, b=1.408 nm, c=0.314 nm) and MgO (ICDD Card No: 01-079-0612, Bravais lattice: face-centred cubic, a=b=c=0.422 nm) phases are observed in the microstructure. Besides, Nb<sub>2</sub>O<sub>5</sub> and Mg totally disappeared in the XRD patterns of the 2 h of milled powders. This indicates that a solid-state reaction took place between the raw materials of Nb<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub> and Mg resulting in the niobium boride phases in three different compositions. Unlike the ideal reduction reaction (3.2) which yields the NbB<sub>2</sub> phase as a main reaction product, NbB<sub>2</sub> is not the dominant phase in the microstructure of the milled powders. Already, the occurrence of niobium borides in different stoichiometry is expected. Absence of dominance in the NbB<sub>2</sub> phase can be attributed to the proposed Nb-B binary phase diagrams in the literature, in which NbB (T<sub>m</sub>≈2800°C, 50 at. % Nb), Nb<sub>3</sub>B<sub>4</sub> (T<sub>m</sub>≈2900°C, 43 at. % Nb) and NbB<sub>2</sub> (T<sub>m</sub>≈3000°C, 25-35 at. % Nb) phases were defined as stable compounds having very close melting points and homogeneity ranges (Rudy and Windisch, 1966; Massalski, 1990; Okamoto, 2008).

It is also understandable that products of the actual reaction triggered by the mechanical milling which is away from the equilibrium conditions may not completely conform to those of the ideal case. Since mechanochemical synthesis process is a kind of mechanical alloying induced by redox/reduction reactions, the formation of products is favorable at the contact points of the particles during repeated collisions. Once NbB, Nb<sub>3</sub>B<sub>4</sub> and NbB<sub>2</sub> phases formed in the sequence of requiring lower amount of boron after milling for 2 h, this variety in stoichiometry did not change. It was already reported that single-phase niobium boride could not be obtained via combustion synthesis of elemental powder compacts even though specific ratios of elemental Nb and B were used as the initial compositions according

to the Nb-B binary phase diagram (Yeh and Chen, 2006). The variety in the stoichiometry of niobium borides can be attributed to some kinetic factors and the non-equilibrium conditions of mechanochemical and combustion synthesis processes (Suryanarayana, 2001). Studies in the current literature showed that the single phase of niobium borides (without any remaining Nb or B) could be achieved by applying high or low temperature processes at steady-state conditions (Motojima et al, 1975; Matsudaira et al, 1989; Cai et al, 2005; Jha et al, 2011; Ma et al, 2009). Moreover, the formation of niobium borides with major NbB and minor NbB<sub>2</sub> and Nb<sub>3</sub>B<sub>4</sub> phases by mechanochemistry of oxide raw materials at room temperature can be different from some other studies which used elemental starting materials and indicated the NbB<sub>2</sub> as the dominant boride phase (Iizumi et al, 2006; Jafari et al, 2015). Due to the fact that mechanochemical synthesis is a room temperature method without applying any external heat, the formed NbB, Nb<sub>3</sub>B<sub>4</sub> and NbB<sub>2</sub> phases keep their presence in the powders and have no chance to transform to a single-phase form after the reaction took place at 2 h of milling.

Although niobium borides were achieved after milling for 2 h, milling was extended up to 9 h in order to detect any probable degradation of the current reaction products and any formation of a new phase. According to the XRD patterns in Figure 4.16, there is an observable broadening in the intensities of the niobium boride and MgO phases by extending milling time up to 9 h which represents a decrease in their crystallite sizes. On the other hand, there are no remaining elemental Nb or B and no additional compounds between Nb-Mg, B-Mg, Nb-Mg-O, Nb-B-O, B-Mg-O, etc. in the detection limit of XRD. In a study by Iizumi et al (2006) related to the mechanical alloying of Nb and B mixtures, NbB<sub>2</sub> was obtained after 20 h of milling but unreacted Nb and B still remained in the structure. Only after prolonging the milling time to 50 h, the XRD peaks of the Nb phase disappeared and a single phase of NbB<sub>2</sub> was obtained in their investigation (Iizumi et al, 2006). However, it should be stated that their process is not an economically feasible way to produce niobium boride powders since it requires high energy consumption due to the very long milling times and high costs of elemental starting materials. In this case, only replacement reaction was induced by mechanical milling of the Nb and B powder particles (Iizumi et al, 2006). In the present study, however, both reduction and replacement reactions took place by using Nb<sub>2</sub>O<sub>5</sub> and B<sub>2</sub>O<sub>3</sub> with the presence of Mg

which initiated the spontaneous ignition between the particles without any external applied heat and hence shortened the overall reaction time. Actually, the impact energy obtained with the collisions of the milling balls, milling walls and powder particles results in a repeated fracture, friction and welding mechanism during the process (Chen et al, 1997; Murty and Ranganathan, 1998; Suryanarayana, 2001; Takacs, 2002; Wieczorek-Ciurowa, 2007). This mechanical energy accumulates in the system, heat conductivity of the milling medium provides the formation of hot spots and mechanical energy converts into chemical energy which proceeds the synthesis process by an explosive reaction (Chen et al, 1997; Murty and Ranganathan, 1998; Suryanarayana, 2001; Takacs, 2002; Wieczorek-Ciurowa, 2007). Large amount of heat released at the time of the explosive and intensive exothermic reaction which proceeds spontaneously and provides the reduction of the reactants until whole Mg converts into MgO. This phenomenon could increase the possibility of yielding products in different stoichiometry. Thus, the products of this highly exothermic reaction are not the same with the theoretical one in reaction (3.2) which is based on the equilibrium conditions.

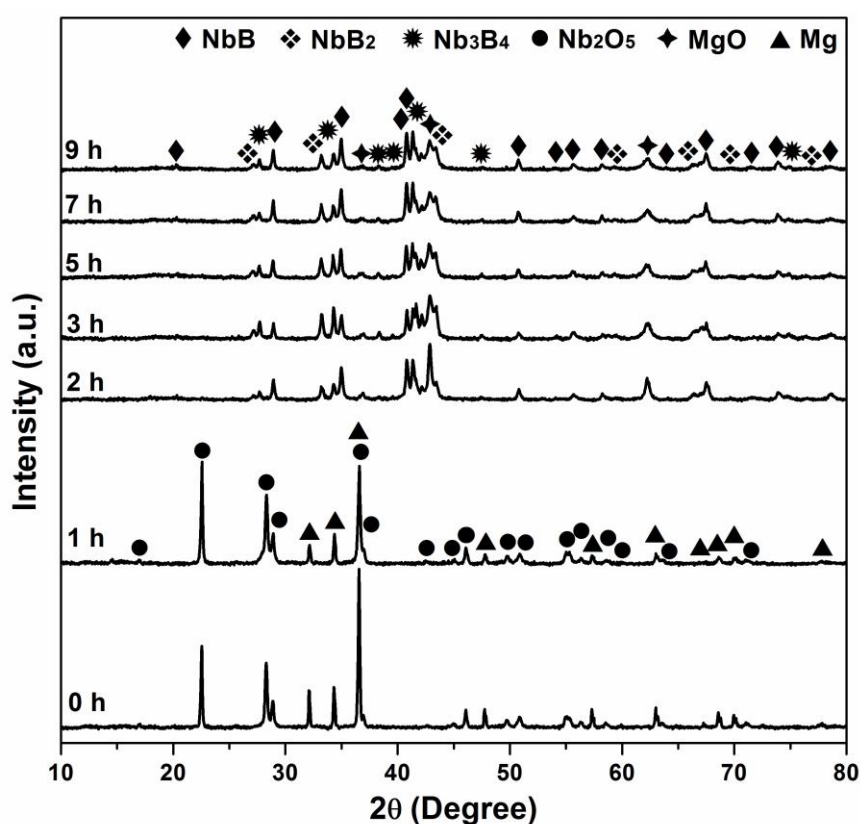


**Figure 4.16 :** XRD patterns of the as-blended  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders and those milled for different times.

In order to determine thermal behavior of the Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-Mg powder blends, DSC analyses were conducted on the milled (1, 2, 3, 5, 7 and 9 h) samples (Figure 4.17). The DSC scan of the powders milled for 1 h shows a sharp exotherm peak at about 650°C, a small narrow exotherm peak at about 760°C and a small broad endotherm peak at about 1300°C. Although 1 h milled powders contain Nb<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub> and Mg phases (Figure 4.16), endothermic peaks corresponding to the melting of B<sub>2</sub>O<sub>3</sub> at 450°C, the melting of Mg at 650°C and the boiling of residual Mg at 1090°C cannot be detected from the DSC scans. The sharp exothermic peak at about 650°C emerges as a result of Nb<sub>2</sub>O<sub>5</sub> reduction by Mg and Mg oxidation. In other words, Mg considerably oxidized to form MgO at 650°C before reaching its melting and boiling points. Consequently, elemental Nb phase formed due to this instantaneous oxidation/reduction phenomenon. Moreover, the small narrow exotherm peak at about 760°C corresponds to the formation of B particles subsequent to the oxidation of Mg. It can be said that a replacement reaction between B<sub>2</sub>O<sub>3</sub> and Mg takes place and it enables to occur free B particles which afterwards participate into the boride formation. These exotherm behavior emerged from the magnesiothermic reduction of B<sub>2</sub>O<sub>3</sub> was also reported at nearly ~800°C in the DTA experiments of Mg-B<sub>2</sub>O<sub>3</sub>-Nb-C and Mg-B<sub>2</sub>O<sub>3</sub>-Nb systems (Jafari et al, 2015; Torabi et al, 2015). Moreover, the proposed reactions' sequence in this study is consistent with the thermodynamic evaluations: The free energies of the formation of Nb (originated from the reduction of Nb<sub>2</sub>O<sub>5</sub> by Mg) and B (originated from the reduction of B<sub>2</sub>O<sub>3</sub> by Mg) were calculated as  $\Delta G^{\circ}_{298} = -1090$  and  $-515$  kJ, respectively. Thus, the small broad endothermic peak at about 1300°C corresponds to the formation of niobium boride phases due to reactions between Nb and B particles. On the other hand, DSC scans of the 2, 3, 5, 7 and 9 h of milled powders (Figure 4.17) do not have any exothermic and endothermic peaks corresponding to the formations of MgO, Nb and B phases because they already comprise NbB, NbB<sub>2</sub>, Nb<sub>3</sub>B<sub>4</sub> and MgO phases after mechanochemical synthesis (Figure 4.16). 2 h of milled powders show an endotherm having an onset temperature at about 1305°C and a maximum peak point at about 1345°C. The onset temperature of this endotherm almost intersects the endothermic peaking point of the powders milled for 1 h. Thus, it can be attributed to the overlapped peak of niobium boride formation originated from remaining Nb which is under the detection limit of XRD (< 2 wt.%) and to the transformation of niobium boride phases. The peak overlapping is understandable because the reaction took

place after 2 h and whole amount of reduced Nb may not contribute to the boride formation. When milling time increased to 3 h, the endotherm became smaller and narrower than that of 2 h milled powders and its peak point shifted to 1370°C, which only indicates the phase transformation of niobium borides. This implies the completion of the boride formation reaction with no evidence of unreacted Nb. As milling time prolonged up to 9 h, the endotherm transformed into a sharper peak than those milled for shorter times without changing its maximum temperature point due to the smaller-sized NbB, NbB<sub>2</sub> and Nb<sub>3</sub>B<sub>4</sub> particles having more reactive surfaces than those milled for shorter times.

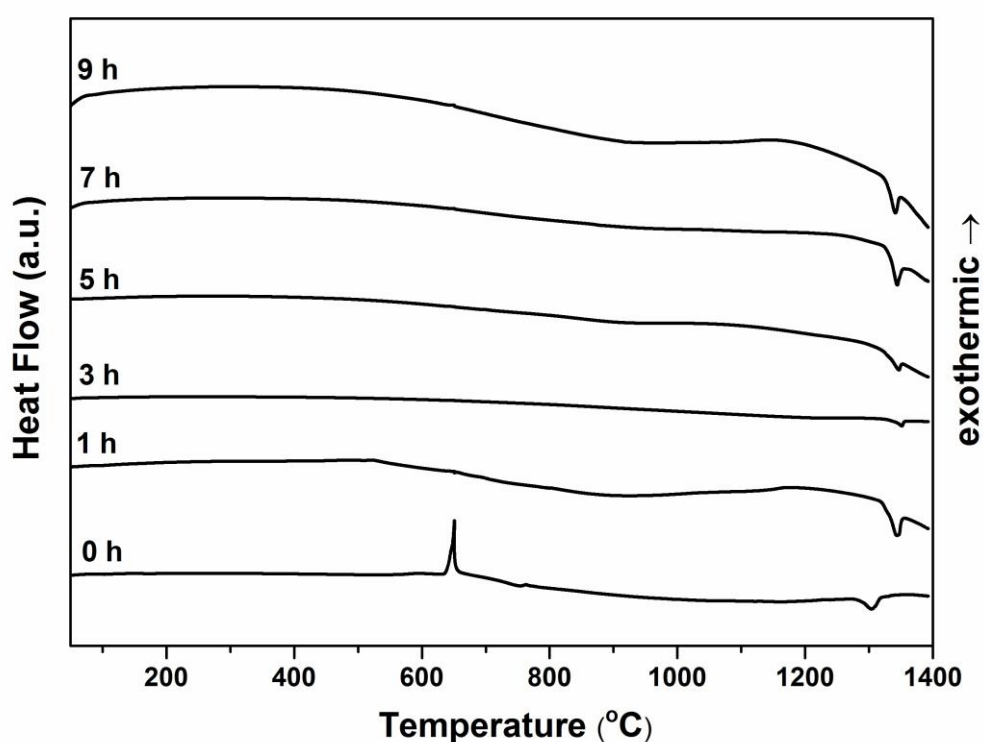


**Figure 4.17 :** DSC scans of the Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-Mg powders milled for different times.

Figure 4.18 are the XRD patterns of the Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-Mg powders milled for 2, 3, 5, 7 and 9 h after leaching with 4 M HCl. Figure 4.18 reveals that the unwanted by-product MgO was completely removed from the powder blend after leaching with 4 M HCl and pure niobium boride powders comprising NbB, NbB<sub>2</sub> and Nb<sub>3</sub>B<sub>4</sub> phases were obtained. As seen from the XRD patterns of the leached samples, there is no residual chloride, oxychloride or hydroxychloride as leaching products which indicates the effectiveness of the leaching parameters. The dissolution of MgO was also confirmed by AAS analyses of the leach solutions decanted from the residual powders: The amount of Mg in the leach solution increases from 5337 to 8312 ppm,

as the milling time increases from 3 to 9 h. This shows that the dissolution of MgO in HCl was enhanced with the increasing milling times. This phenomenon can be attributed to the higher surface areas of the particles milled for longer times (Suryanarayana, 2001).

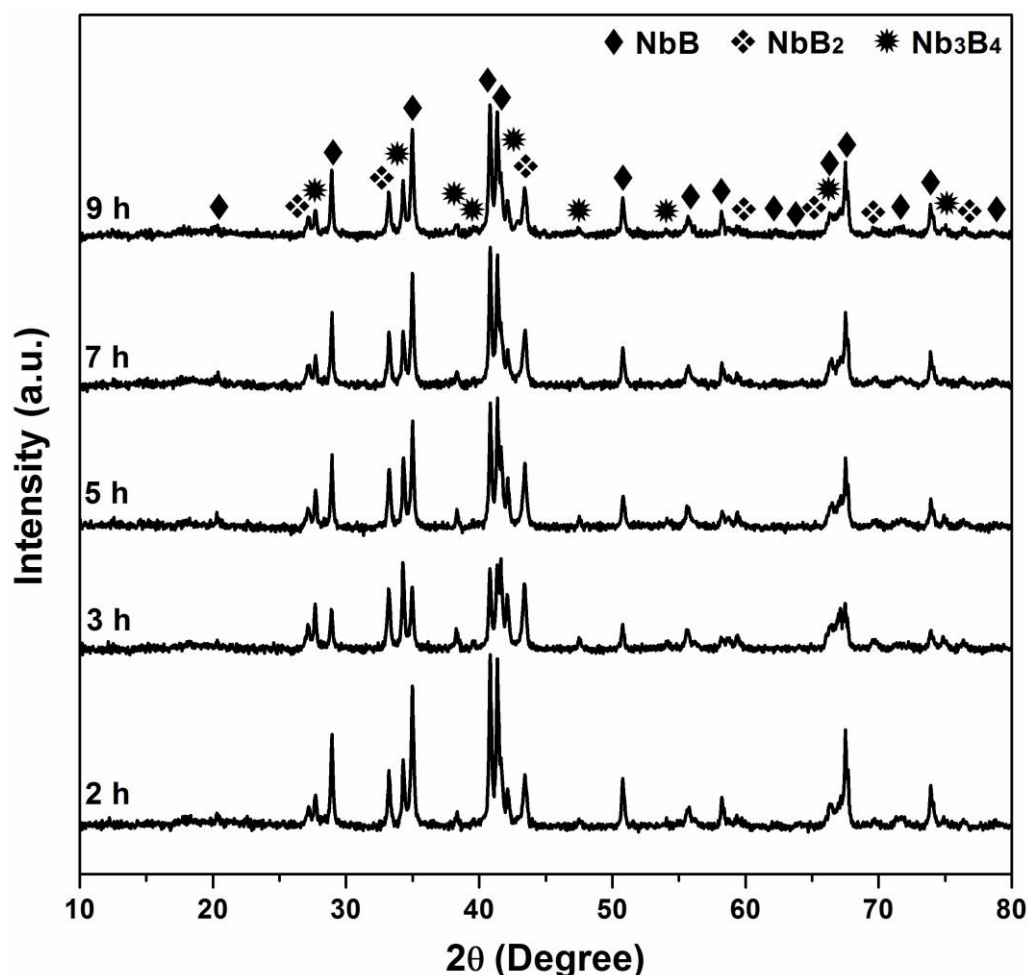


**Figure 4.18 :** XRD patterns of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for different times after leaching with HCl.

Furthermore, AAS analyses of the leach solution showed that it consists of 35 ppm Fe for the powders milled for 5 h after leaching with HCl. The remaining Fe impurity in the powders can also be determined from the magnetic measurements, provided that the material has a ferromagnetic tendency. Figure 4.19(a)-(b) exhibit the room-temperature magnetic field versus magnetization curve of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 5 h before and after leaching with 4 M HCl. The 5 h of milled powders are paramagnetic (Figure 4.19(a)) which points out the Fe impurity in the order of ppm. As seen from Figure 4.19(b), mechanochemically synthesized niobium boride powders ( $\text{NbB-NbB}_2\text{-Nb}_3\text{B}_4$ ) are diamagnetic which definitely proves the

absence of Fe in the resultant powders. Both the AAS analysis and magnetic measurements indicate that Fe impurity released from the milling media was completely removed by HCl leaching as well as MgO.

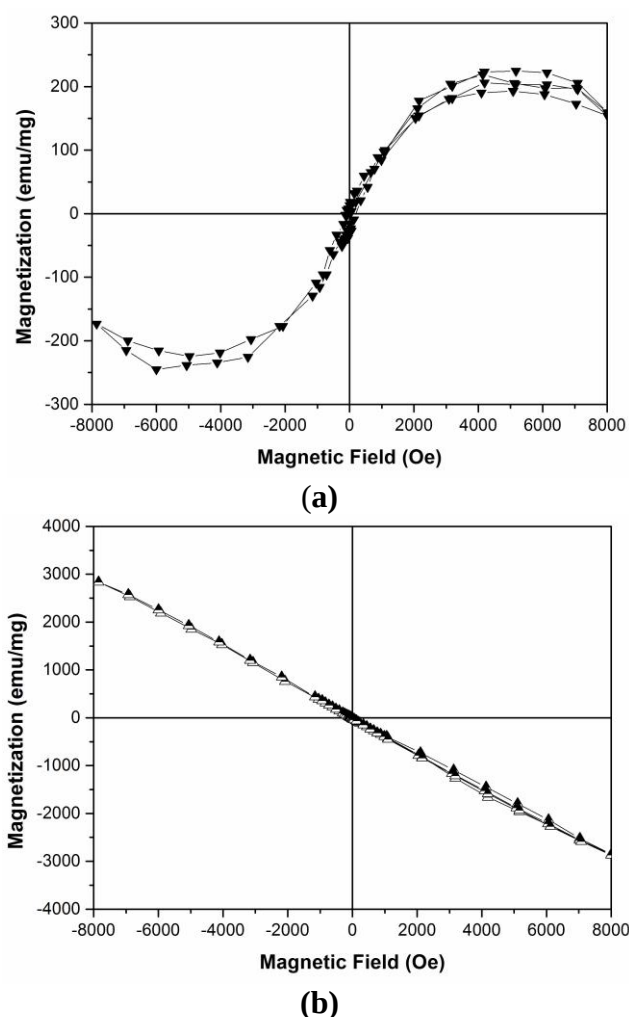


**Figure 4.19 :** Room-temperature magnetic measurement of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 5 h: (a) before leaching and (b) after leaching with 4 M HCl.

Table 4.2 exhibits the semi-quantitative phase analyses of the powders milled for different times after leaching obtained from the Rietveld refinement method based on their XRD patterns given in Figure 4.18. Rietveld refinement method was conducted on the milled and leached powders for the determination of the estimated amounts of the niobium boride phases eliminated from the MgO contamination. As seen from Table 4.2, extended milling times up to 9 h seem to change the compositions of the leached products: the amounts of NbB, NbB<sub>2</sub> and Nb<sub>3</sub>B<sub>4</sub> phases differ from one another at each milled powder. After reduction reaction took place at the end of milling for 2 h, NbB emerged as the dominant phase with 55 vol. %. However,

$\text{Nb}_3\text{B}_4$  occurred as the major phase with 43.3 vol. % at the end of milling for 3 h. Besides, the amounts of  $\text{NbB}_2$  and  $\text{Nb}_3\text{B}_4$  phases gradually decreased and  $\text{NbB}$  phase had the majority in the total volume by increasing milling time from 3 to 9 h. The change of dominant phase in the 2 and 3 h of milled powders arose from the incidental conditions of the mechanochemical synthesis process such as interaction of reactant particles at  $\text{B}_2\text{O}_3$ -poor or  $\text{B}_2\text{O}_3$ -rich surfaces until a homogeneous distribution was reached. Thus, it can be said that a steady-state condition in the overall reaction could be achieved at milling times over 3 h, at which a consistency in the major phase was obtained. These findings are also in good agreement with the XRD and DSC analyses in Figures 4.16, 4.17 and 4.18. Thus,  $\text{NbB}$  is the dominant phase after milling for 5, 7 and 9 h and subsequent leaching.

**Table 4.2 :** Semi-quantitative phase analyses of the powders milled for different times after leaching obtained from the Rietveld refinement method based on their XRD patterns.

| Milling Time (h) | Amounts of Phases (vol.%) |                  |                                |
|------------------|---------------------------|------------------|--------------------------------|
|                  | NbB                       | NbB <sub>2</sub> | Nb <sub>3</sub> B <sub>4</sub> |
| 2                | 55.0                      | 15.9             | 29.1                           |
| 3                | 29.8                      | 26.9             | 43.3                           |
| 5                | 43.2                      | 22.1             | 34.7                           |
| 7                | 52.2                      | 21.4             | 26.4                           |
| 9                | 55.0                      | 19.4             | 25.6                           |

Figure 4.20 presents the DSC scans of the  $\text{Nb}_2\text{O}_5$ - $\text{B}_2\text{O}_3$ -Mg powders milled for 5 and 9 h after leaching with 4 M HCl. They almost show the same tendency up to 1300°C. DSC scans of the milled and leached powders given in Figure 4.20 do not show any sharp exothermic peak. This is the solid evidence of sufficient purity that milled powders achieved after leaching with 4 M HCl. Even if a small amount of MgO (which cannot be detected by XRD) were still present in the leached powders, it would react with niobium boride phases to form  $\text{Mg}_x\text{Nb}_y\text{O}_z$  compound during the heating up to 1300°C, which is a highly exothermic reaction. On the basis of XRD, AAS, DSC analyses and magnetic measurements of the milled powders after leaching treatment, it is clear that the resultant powders do not include any contamination or other unwanted reaction products. Furthermore, DSC scans in Figure 4.20 show decrease in heat flow values at temperatures higher than 1200°C. To determine the cause of this decrease, milled and leached powders were annealed at 1500°C for 4 h which is over the heating capability of the calorimeter.

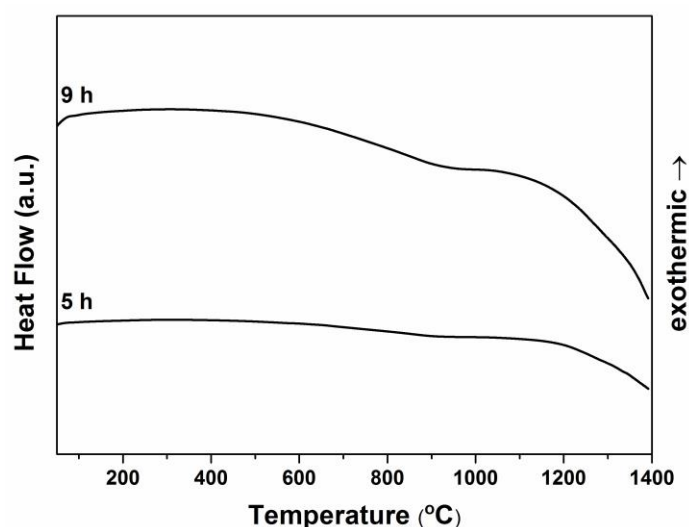


**Figure 4.20 :** DSC scans of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 5 and 9 h after leaching.

Figure 4.21 is the XRD pattern of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 5 h after leaching with 4 M HCl and annealing at  $1500^\circ\text{C}$  for 4 h. Figure 4.21 clearly shows that after annealing process, NbB, NbB<sub>2</sub> and Nb<sub>3</sub>B<sub>4</sub> containing powders completely transform to the NbB phase which was already dominant in the microstructure after leaching treatment (Table 4.2). Thus, the sharp decrease in the heat flow corresponds to the NbB phase transformation at high temperature. X-ray reflections for the NbB phase (ICDD Card No: 32-0709, Bravais lattice: base-centered orthorhombic,  $a=0.330$  nm,  $b=0.872$  nm,  $c=0.317$  nm) contain 17 peaks at values of  $2\theta=10\text{-}80^\circ$  which are indexed as the {020}, {110}, {021}, {111}, {130}, {131}, {200}, {002}, {150}, {022}, {060}, {112}, {151}, {061}, {240}, {042} and {241} families of planes.

On the other hand, the microstructure of the 3 h milled and leached powders (Figure 4.18) remain the same after annealing at  $1500^\circ\text{C}$ , which presents niobium boride phases with different compositions. This indicates that milling for 3 h does not provide sufficient energy for the complete transformation of niobium boride phases during annealing. It has been already reported that mechanical milling changes the homogeneity and reactivity of powder particles (Suryanarayana, 2001). Activation energy absorbed by the particles during milling assisted the phase transformation of the Nb borides. The absorbed activation energy after 3 h of milling is not adequate for the reaching of the energy barrier towards the complete transformation whereas enough activation energy produced after 5 h triggered the complete phase

transformation during heat treatment (Chen et al, 1997; Suryanarayana, 2001). Since NbB, NbB<sub>2</sub> and Nb<sub>3</sub>B<sub>4</sub> phases are all very stable niobium boride phases with close melting points (2800-3000°C) according to the Nb-B phase diagram, the phase change mechanism can also be explained by isothermal annealing condition of highly activated boride powders during 4 h of holding time (Rudy and Windisch, 1966; Massalski, 1990). This is well known that the mechanical activation of the powder particles and subsequent annealing enables the activated particles to react at lower temperatures than thermodynamically required (Suryanarayana, 2001).

Thus, a deformation-induced NbB single phase could only be obtained after milling for 5 h and subsequent annealing (Figure 4.21). This might be the result of the reaction between niobium boride phases with low Nb contents (Nb<sub>3</sub>B<sub>4</sub>, NbB<sub>2</sub>) to yield NbB phase with high Nb content releasing small amount of B. However, the diffraction peaks of B cannot be detected by XRD analysis due to its amorphous structure or probable incorporation of small B atoms into orthorhombic NbB structure.

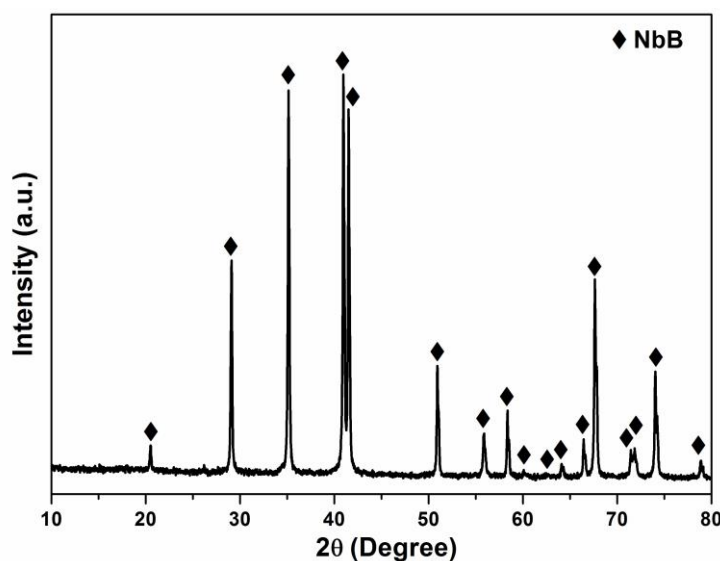


**Figure 4.21 :** XRD patterns of the Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-Mg powders milled for 5 h after leaching and annealing at 1500°C.

Figure 4.22(a)-(c) show the SM images of the as blended Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-Mg powders and those milled for 5 h, before and after leaching. As Figure 4.22(a) and (b) compare to each other, the difference between the as-blended and milled powders can be clearly seen: As blended powders contain the mixtures of Nb<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub> and Mg particles in granular form, whereas 5 h of milled powders consist of

agglomerated NbB, NbB<sub>2</sub>, Nb<sub>3</sub>B<sub>4</sub> and MgO particles according to their XRD patterns (Figure 4.16). After leaching with 4 M HCl and hence the removal of MgO phase (Figure 4.22(c)), the particles were liberated and their colours became relatively darker. SM image of the powders milled for 5 h after HCl leaching (Figure 4.22(c)) promotes the complete purification of the niobium boride powders without any contamination, as considered along with its XRD pattern given in Figure 4.18.

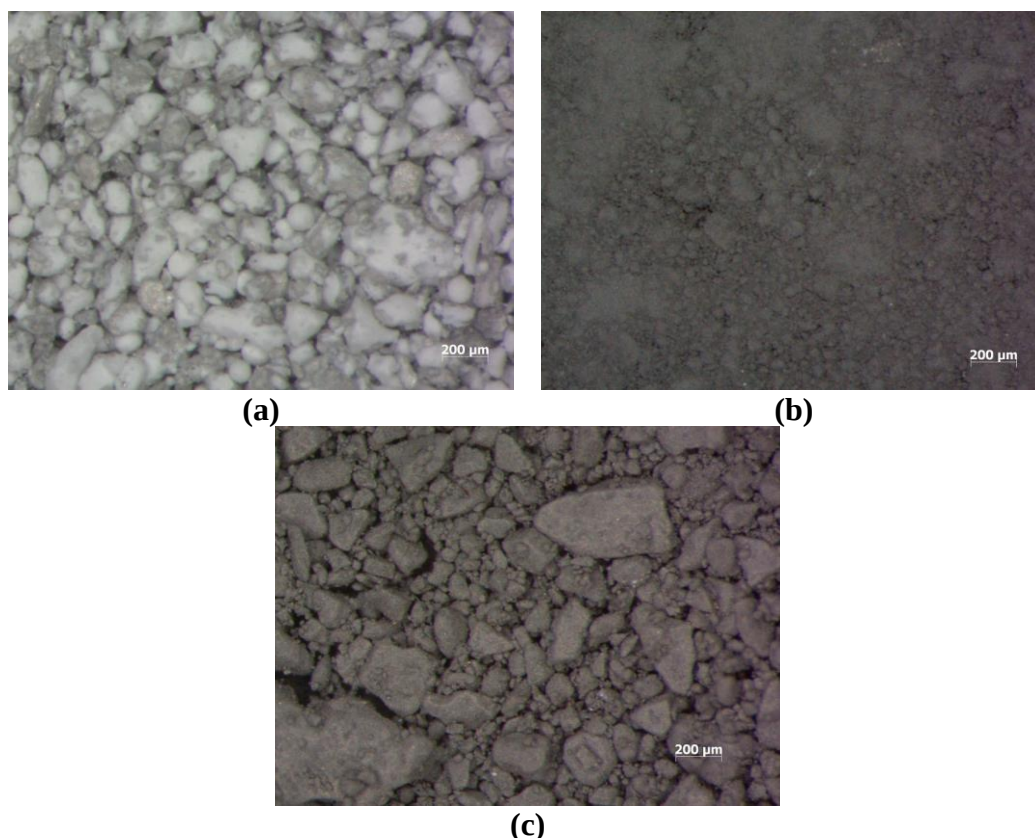


**Figure 4.22 :** SM images of the as blended Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-Mg powders and those milled and leached powders: (a) as-blended powders, (b) powders milled for 5 h and (c) powders milled for 5 h after leaching.

In order to show the effect of mechanical milling on the surface areas and particle sizes of the powders, the BET surface area measurements were conducted on the as-blended Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-Mg powders and those milled for 3 and 5 h (Figure 4.23(a)). It is evident from Figure 4.23(a) that surface area of the as-blended powders drastically increase from 2.46 to 6.35 m<sup>2</sup>/g after milling for 3 h, indicating a significant decrease in their particle sizes. Additional milling of 3 h increases the surface area value from 6.35 to 7.54 m<sup>2</sup>/g. Figure 4.23(b) shows the particle size distribution of the Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-Mg powders after milling for 5 h. The average particle size of the 5 h of milled powders is 538 nm. The data obtained from the particle size measurement given in

Figure 4.23(b) revealed that 10 vol. % amount of the total powders has an average particle size of about 1.7  $\mu\text{m}$ . These larger particles can be attributed to the MgO phase in the structure of the 5h of milled powders. As the particle sizes of the initial powders are considered ( $\text{Nb}_2\text{O}_5$ :20  $\mu\text{m}$ ,  $\text{B}_2\text{O}_3$ :470  $\mu\text{m}$  and Mg:145  $\mu\text{m}$ ), it is obvious that a significant particle size refinement was provided by reducing the micron-scale starting powders to nano-scales by mechanical milling for 5 h.

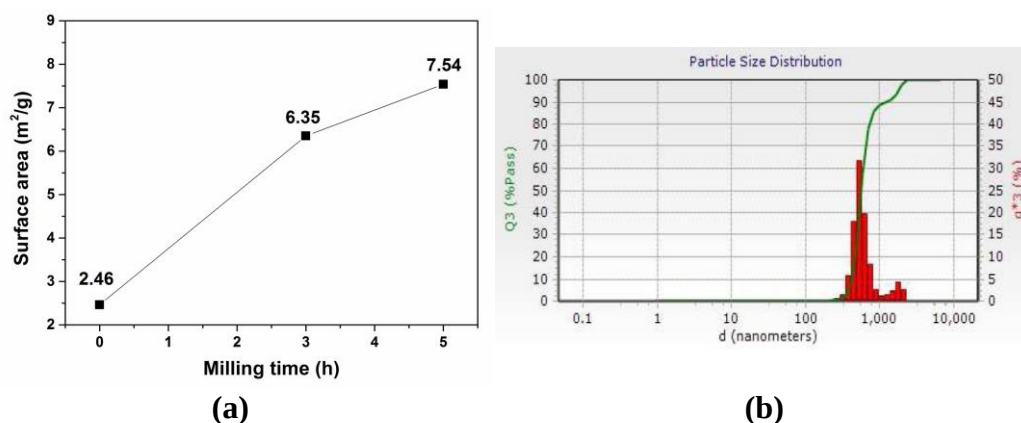


**Figure 4.23 :** Surface area and particle size measurements of the as-blended and milled powders: (a) surface areas of the as-blended  $\text{Nb}_2\text{O}_5$ - $\text{B}_2\text{O}_3$ -Mg powders and those milled for 3 and 5 h and (b) particle size distribution of the  $\text{Nb}_2\text{O}_5$ - $\text{B}_2\text{O}_3$ -Mg powders milled for 5 h.

Figures 4.24(a)-(d) show the particle size distributions of the milled powders after leaching with 4 M HCl, i.e. the resultant NbB-NbB<sub>2</sub>-Nb<sub>3</sub>B<sub>4</sub> powders. The graphs in Figure 4.24(a) through (d) display the average sizes of the leached particles as about 219, 194, 197 and 166 nm for the powders milled for 3, 5, 7 and 9 h after leaching, respectively. Milling of the  $\text{Nb}_2\text{O}_5$ - $\text{B}_2\text{O}_3$ -Mg powder blends for 3 h resulted in a significant decrease in the particle sizes from micro to nano-scales, even after the leaching process. Additional milling of 6 h reduces the particle sizes from 219 to 166 nm in the resultant powders. The obtained average particle size values of the milled and leached powders are in consistent with the surface areas of the milled powders given in Figure 4.23(a). Moreover, as Figure 4.23(b) and 4.24(b) compare to each other, it can be said that the elimination of large MgO particles provided a significant decrease in average particle sizes from 538 to 194 nm after leaching with 4 M HCl. In overall, the results of the surface areas of the milled powders (Figure 4.23(a)) and particle sizes for the milled and leached powders (Figures 4.23(b) and 4.24) show that high energy ball milling is an effective way to obtain small particles from large starting materials.

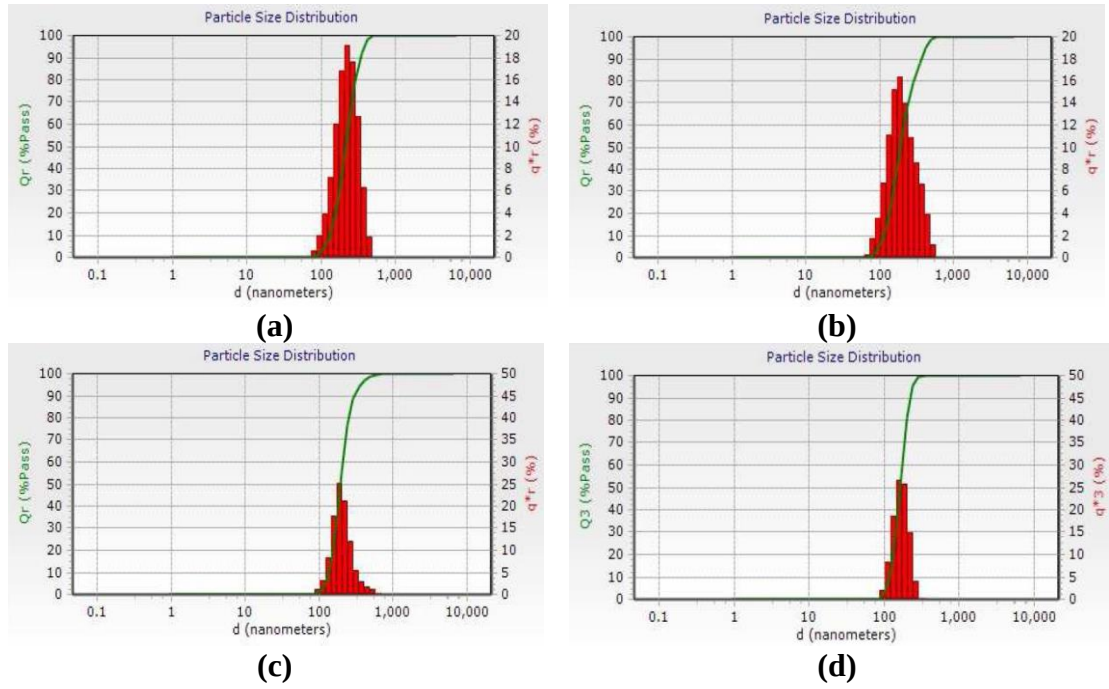


**Figure 4.24 :** Particle size distributions of the milled  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders after leaching: (a) 3 h, (b) 5 h, (c) 7 h and (d) 9 h.

Figures 4.25(a)-(d) are the respective secondary electron SEM images of the as-blended  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders, those milled for 5 h and those milled for 5 h after leaching with 4 M HCl and those milled for 5 h after leaching with 4 M HCl and annealing at  $1500^\circ\text{C}$ . As seen from Figure 4.25(a), as-blended powders have irregular agglomerates and spherical and leaf-like particles. Figure 4.25(b) reveals that microstructure of the powders milled for 5 h involves spherical-shaped niobium boride particles embedded in blurred MgO particles, in agreement with the XRD patterns in Figure 4.16. Figure 4.25(b) clearly shows the adherence and agglomeration of the particles due to the heat released by the mechanochemical reaction. The microstructure of the powders after milling for 5 h and subsequent leaching given in Figure 4.25(c) exhibits a homogenous particle distribution and consists of equiaxed particles smaller than 700 nm in the absence of the MgO phase with blurred microstructure. However, agglomeration of the powder particles prevents the observation of the smaller ones. Therefore, particle size measurement carried out after homogenization of the powder blends gives more accurate results as about 190 nm, as previously presented in Figure 4.24(b). Figure 4.25(d) shows the microstructure of the powders milled for 5 h after leaching with 4 M HCl and annealing at  $1500^\circ\text{C}$  for 4 h, indicating the effect of heat treatment and hence phase transformation (from niobium borides comprising NbB, NbB<sub>2</sub> and Nb<sub>3</sub>B<sub>4</sub> phases to

the single phase NbB) on the morphologies of the particles (Figure 4.21). It can be seen from Figure 4.25(d) that annealed powders consist of distinct particles with relatively clear boundaries which are larger than those of the milled and leached ones (Figure 4.25(c)).

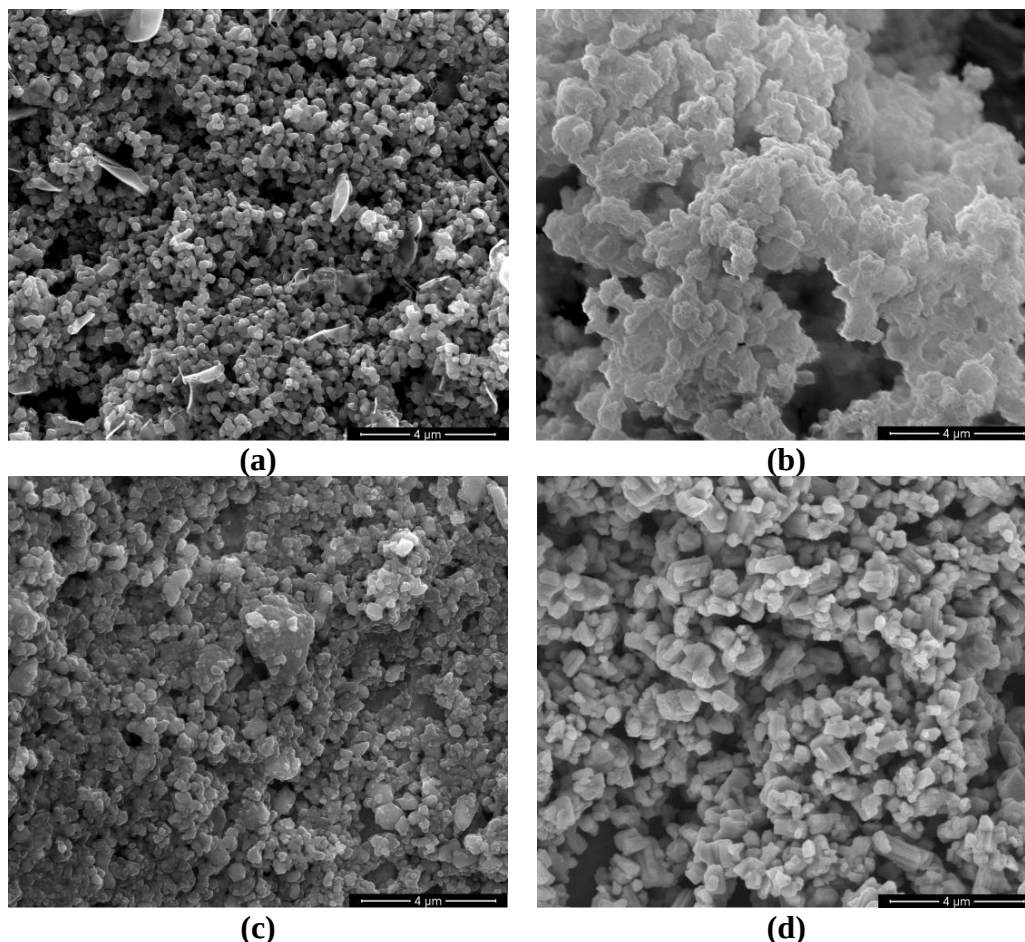


**Figure 4.25 :** SEM images of the as-blended Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-Mg powders and those after milling, leaching and annealing processes: (a) as-blended powders (0 h), (b) powders milled for 5 h, (c) powders milled for 5 h after leaching and (d) powders milled for 5 h after leaching and annealing at 1500°C.

In order to show the effect of annealing on the microstructure of the resultant powders clearly, SEM images of the Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-Mg powders milled for 5 h after leaching and milled for 5 h after leaching and annealing at 1500°C in higher magnifications are presented in Figure 4.26(a)-(b). Figure 4.26(a) and (b) show respectively the powders containing NbB-NbB<sub>2</sub>-Nb<sub>3</sub>B<sub>4</sub> phases and NbB single phase powders, according to their XRD patterns (Figures 4.18 and 4.21). The microstructure of the powders after milling and leaching presents the similar morphology as previously obtained from that of the mechanochemically synthesized

boride powders (Çamurlu, 2011; Coşkun and Öveçoğlu, 2013; Ağaoğulları, 2014; Torabi et al, 2015). Torabi et al (2015) reported that the agglomeration occurs in the mechanochemically synthesized powders in order to diminish surfaces and decrease the surface energy. On the other hand, during annealing, residual stresses are relieved by recovery and recrystallization stages (Thümmeler and Oberacker, 1993). Therefore, as seen from Figure 4.26(b), the particles were liberated and grain growth occurred due to the partial sintering of the powder particles.

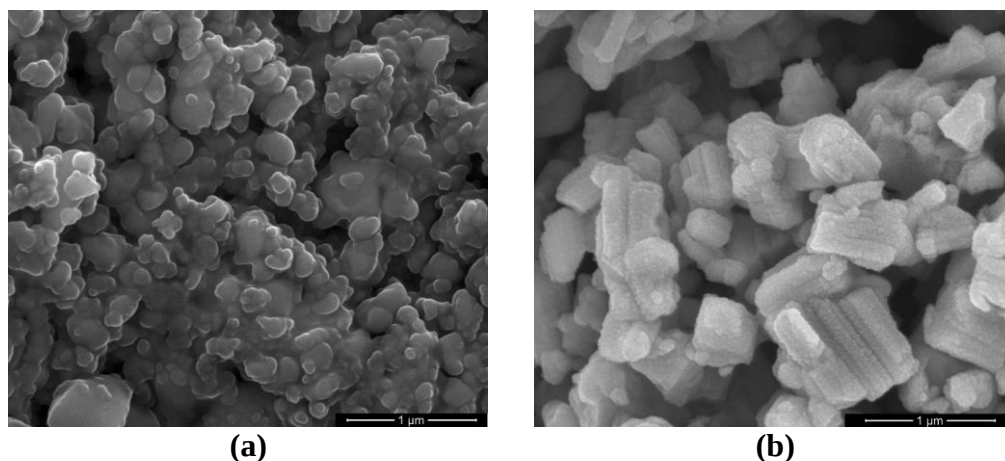


**Figure 4.26 :** SEM images of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 5 h (80000X): (a) after leaching and (b) after leaching and annealing at  $1500^\circ\text{C}$ .

In order to reveal the phase distribution clearly, SEM/EDX analyses were carried out on compacted pellets of the powders. Figures 4.27(a)-(e) show the SEM/EDX analyses of the pellet obtained from the compaction of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 5 h. Figures 4.27(b) through (e) present the associated elemental maps for Nb, B, Mg and O taken from the pellet of the 5 h milled powders. Figure 4.27(c) reveals the uniform distribution of the B particles with weak signals since they are suppressed by the other strong signals of the elements. The elemental Mg map (Figure 4.27(d)) coincides almost entirely with the elemental O map (Figure 4.27(e)), suggesting the presence of the MgO phase. The elemental Nb map (Figure 4.27(b)) fulfills the gaps in the Mg and O maps and also coincides with the Mg and O elemental maps at the some regions. Thus, the distribution of the Nb, B, Mg and O elements throughout the microstructure reveals the adherence and simultaneous existence of niobium boride and MgO phases which is also in good agreement with the blurred morphology of the milled powders given in Figure 4.25(b). Furthermore, SEM/EDX analyses of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 5 h confirms the phase analyses obtained by XRD (Figure 4.16).

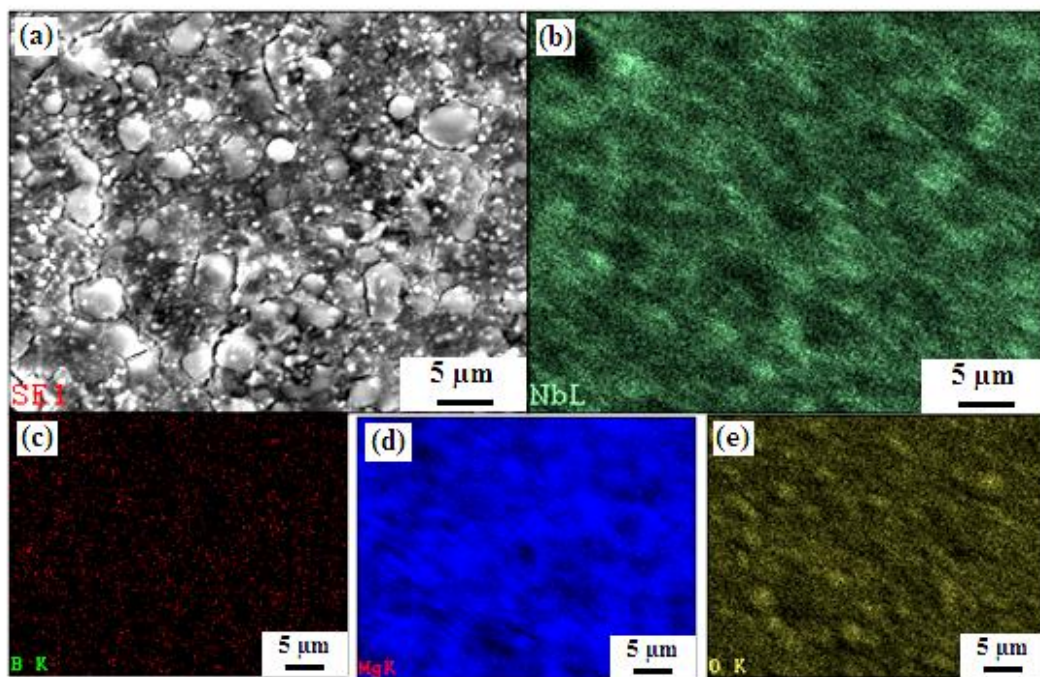


**Figure 4.27 :** SEM/EDX analyses of the pellet obtained from the compaction of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 5 h: (a) SEM image of the pellet and corresponding elemental maps for (b) Nb, (c) B, (d) Mg and (e) O.

Figure 4.28(a)-(c) show the SEM/EDX analyses of the pellet obtained from the compaction of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 5 h after leaching. Figure 4.28(a) through (c) present the secondary electron SEM image and the associated elemental maps for Nb and B taken from the pellet of the 5 h milled powders after leaching. The elemental Nb map (Figure 4.28(b)) coincides almost entirely with the elemental B map (Figure 4.28(c)), suggesting the presence of a niobium boride phase.

Furthermore, as Figure 4.27(b)-(c) and Figure 4.28(b)-(c) compare to each other, it is clear that the signals arising from Nb and B elements considerably increased after leaching treatment. Besides, any signals of Mg and O were not detected during SEM/EDX analyses of the leached powders. This is the result of the removal of unwanted MgO phase (Figure 4.18) after leaching which also proves the purity of the niobium boride powders.

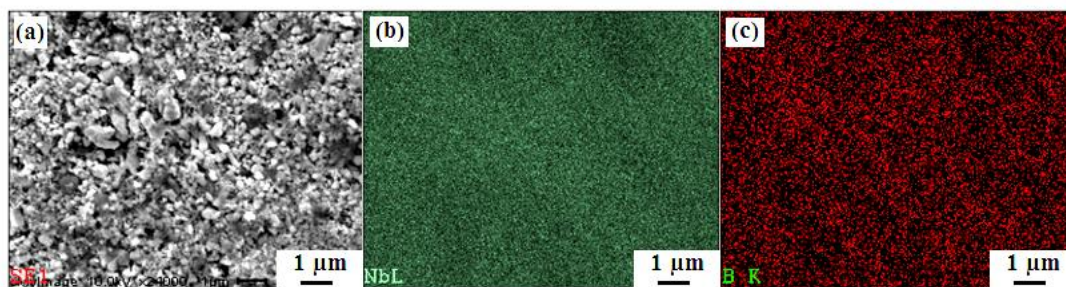


**Figure 4.28 :** SEM/EDX analyses of the pellet obtained from the compaction of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 5 h after leaching: (a) SEM image of the pellet and corresponding elemental maps for (a) Nb and (b) B.

Figure 4.29(a)-(d) show the TEM images of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 5 h after leaching with 4 M HCl. Figure 4.29(a) is a bright-field (BF) image of an equiaxed particle approximately 200 nm in size, which is consistent with the reported average particle size of the leached powders shown in Figure 4.24(b). Selected area diffraction pattern (SADP) taken from this particle in Figure 4.29(b) is a spot pattern which reveals the presence of the orthorhombic NbB phase from a single grain (Camera length is 80 cm and zone axis is  $[\bar{3}12]$ ).

Figure 4.29(c) is a bright-field (BF) image of an ellipsoid particle approximately 600 nm in size, which represents the larger particles in the obtained powders. Selected area diffraction pattern (SADP) taken from this particle in Figure 4.29(d) is a spot pattern which also reveals the presence of the orthorhombic NbB phase from a single grain (Camera length is 80 cm and zone axis is  $[\bar{3}10]$ ). NbB was also detected as the dominant phase in the XRD pattern in Figure 4.18 and semi-quantitative phase analysis in Table 4.2 of the powders milled for 5 h after leaching.

Additional TEM characterizations carried out on other regions of the same grain shown in Figure 4.29(a) revealed spot patterns of single crystalline particles with different zone axes, all belonging to the NbB phase.

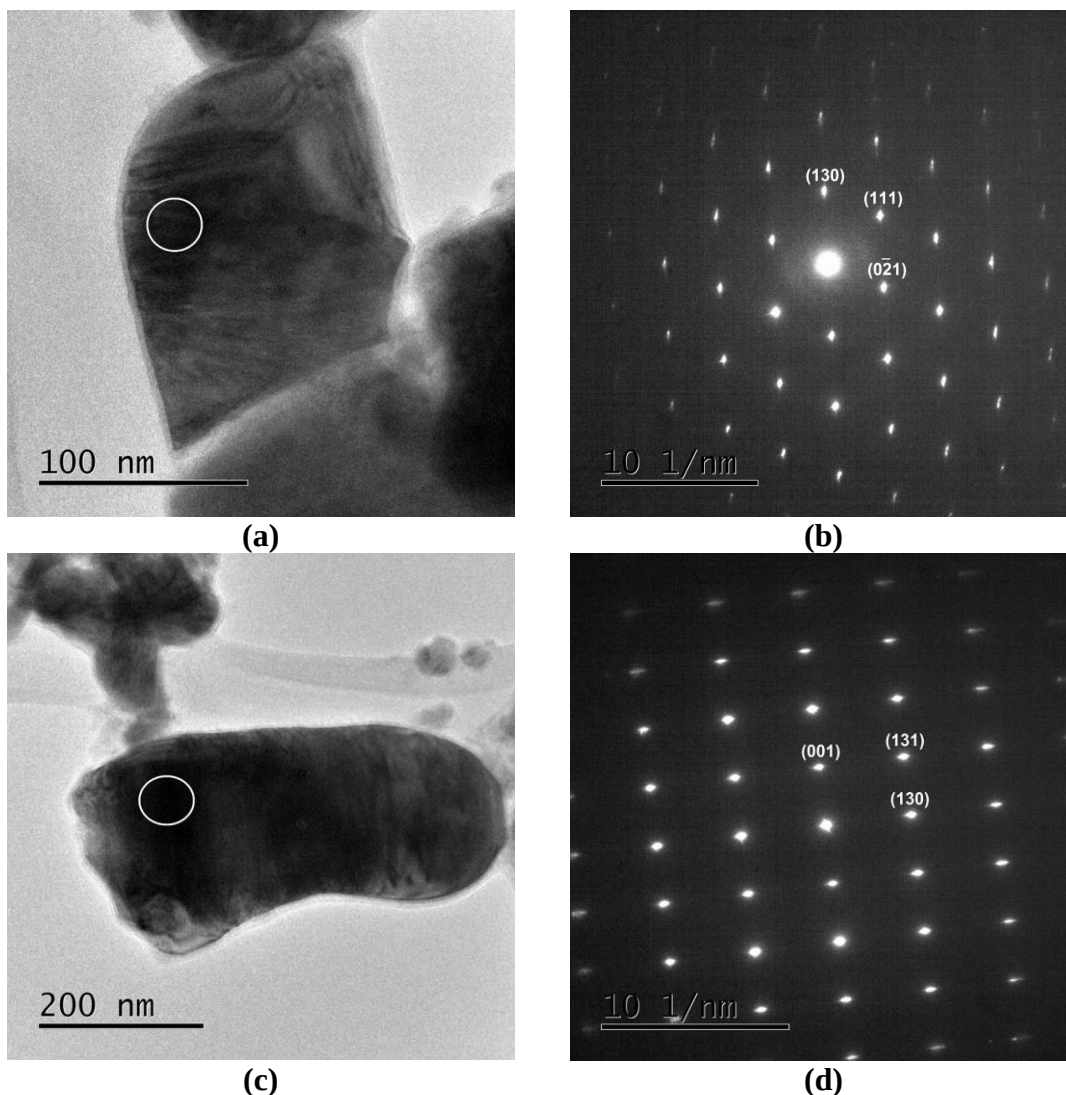


**Figure 4.29 :** TEM images of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 5 h after leaching: (a) bright-field (BF) image, (b) its corresponding selected area diffraction pattern (SADP) revealing the presence of the NbB phase (Camera length is 80 cm and zone axis is  $[\bar{3}12]$ ), (c) bright-field (BF) image and (d) its corresponding selected area diffraction pattern (SADP) revealing the presence of the NbB phase (Camera length is 80 cm and zone axis is  $[3\bar{1}0]$ ).

As a conclusion, niobium boride powders having NbB,  $\text{NbB}_2$  and  $\text{Nb}_3\text{B}_4$  phases in various amounts and single phase NbB powders were successfully synthesized by using solid-state synthesis methods from related metal oxide raw materials in the presence of a strong reducing agent. NbB-NbB<sub>2</sub>-Nb<sub>3</sub>B<sub>4</sub> powders with an average particle size about 190 nm in high purity were obtained in the absence of any intermediate phase and any impurity via mechanochemistry by milling of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders for 5 h and leaching with 4 M HCl. After annealing at 1500°C for

4 h, pure and nano-sized niobium boride powders transformed to a single phase NbB without leaving behind NbB<sub>2</sub> and Nb<sub>3</sub>B<sub>4</sub> phases.

#### **4.3 Milling-Assisted Carbothermal Production of the Niobium Boride-Based Composite Powders**

In this section, the synthesis of NbB<sub>2</sub>-based composite powders containing different amounts of NbC is examined by the mechanical milling-assisted carbothermal reduction of Nb<sub>2</sub>O<sub>5</sub> and B<sub>2</sub>O<sub>3</sub> powder blends. The effects of milling time, annealing temperature and C content on the formation and microstructure of the final products are investigated with the help of XRD, SEM/EDX, TEM, DSC/TG and FTIR analyses. Firstly, the phase and thermal analyses of the powders are presented in the case of using stoichiometric initial materials. The effect of milling and annealing on the reaction mechanism and the microstructure of the obtained powders are presented in the first two separate subsections. At the third subsection, the effects of stoichiometric excess amount of C (100 wt.%) on the reaction products and microstructure are investigated.

Figure 4.30 illustrates the XRD patterns of the as-blended Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-C powders and those milled for 1, 3 and 5 h. As clearly observed from Figure 4.30, there are no reactions between Nb<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub> and C even after milling for 5 h because the Nb<sub>2</sub>O<sub>5</sub> (ICDD Card No: 01-071-0336, Bravais lattice: primitive orthorhombic, a=0.617 nm, b=2.917 nm, c=0.393 nm) and C (ICDD Card No: 056-0159, Bravais lattice: primitive hexagonal, a=b=0.246 nm, c=0.671 nm) phases are still present in the XRD patterns of the powders. It is clear that C peaks broaden and their intensities gradually decrease upon increasing the milling time from 0 to 5 h, indicating a gradual decrease in their crystallite sizes and an increase in their lattice strains. There is an observable decrease in the intensities of the Nb<sub>2</sub>O<sub>5</sub> peaks from 0 to 1 h. However, this decrease is less than that from 1 to 5 h.

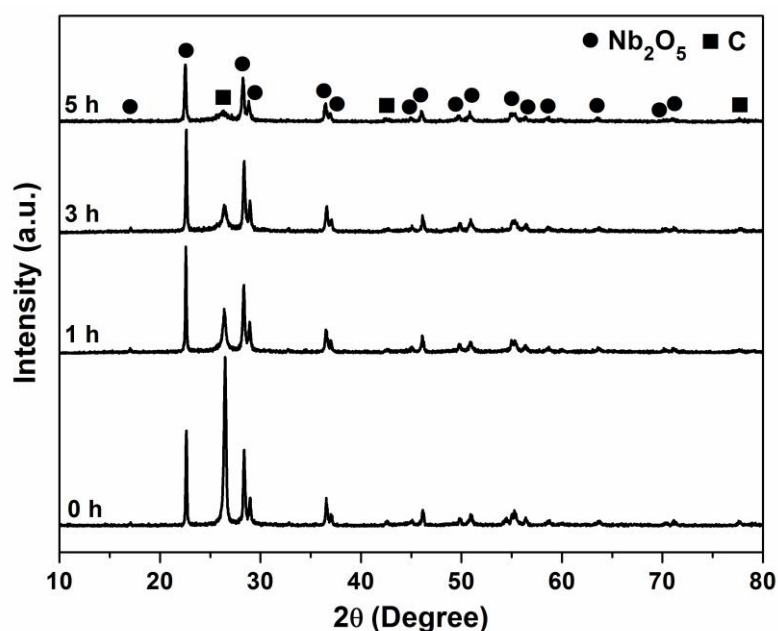


**Figure 4.30** : XRD patterns of the as-blended Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-C powders and those milled for 0, 1, 3 and 5 h.

Table 4.3 exhibits the crystallite sizes and lattice strains of C and Nb<sub>2</sub>O<sub>5</sub> particles obtained from their most intense diffraction peaks as a function of milling time in the powders milled for 0, 1, 3 and 5 h. The crystallite size of C decreases from 68.8 to 3.2 nm by increasing the milling time from 0 to 5 h. Additionally, the lattice strain of C increases from 0.26 to 3.95 % by increasing the milling time from 0 to 5 h. Moreover, the crystallite size of Nb<sub>2</sub>O<sub>5</sub> decreases from 216.2 to 96.3 nm, and its lattice strain increases from 0.08 to 0.25 % by extending the milling time from 0 to 5 h. These results show that much more crystallite refinement and residual strain were obtained in the C particles than in the Nb<sub>2</sub>O<sub>5</sub> particles in the milled powders.

**Table 4.3** : The crystallite sizes and lattice strains of C and Nb<sub>2</sub>O<sub>5</sub> particles in the as-blended powders and those milled for 1, 3 and 5 h.

| Milling Time (h) | Crystallite Size (nm) |                                | Lattice Strain (%) |                                |
|------------------|-----------------------|--------------------------------|--------------------|--------------------------------|
|                  | C                     | Nb <sub>2</sub> O <sub>5</sub> | C                  | Nb <sub>2</sub> O <sub>5</sub> |
| 0                | 68.8                  | 216.2                          | 0.26               | 0.08                           |
| 1                | 24.7                  | 189.6                          | 0.94               | 0.10                           |
| 3                | 9.2                   | 181.1                          | 3.50               | 0.12                           |
| 5                | 3.2                   | 96.3                           | 3.95               | 0.25                           |

Furthermore, no peaks belonging to the B<sub>2</sub>O<sub>3</sub> phase can be observed in the XRD pattern in Figure 4.30, which can be attributed to its amorphous nature. To demonstrate the presence of B<sub>2</sub>O<sub>3</sub> in the powders and to observe its evolution during the milling, FTIR analyses were conducted on the as-blended powders and those

milled for 5 h. Figure 4.31 presents the FTIR spectra of the as-blended powders and those milled for 5 h in the wave number range of 1000 – 4000  $\text{cm}^{-1}$ : IR absorptions at wave numbers of approximately 1200  $\text{cm}^{-1}$  (B-O deformation mode), 1460  $\text{cm}^{-1}$  (B-O stretching mode) and 3228  $\text{cm}^{-1}$  (B-OH mode) are observed (Tsou and Kowbel, 1996; Moon et al, 2004). In addition, weaker absorption peak at 2260  $\text{cm}^{-1}$  (B-H mode) is identified in the FTIR spectra of the as-blended powders (Tsou and Kowbel, 1996; Moon et al, 2004). The formation of B-H and B-OH bonds can be attributed to two reasons such as the presence of an amount of H-B-O containing compounds in the  $\text{B}_2\text{O}_3$  structure and the humidity arisen from the handling of the powders in a laboratory atmosphere, namely physically/chemically adsorbed water to the  $\text{B}_2\text{O}_3$  (Tsou and Kowbel, 1996; Moon et al, 2004). Thus, it is shown that  $\text{B}_2\text{O}_3$  is still present in the powders after milling for 5 h, and the intensities of its peaks become much smaller and broader. The decrease in the absorbance value and the increase in the width of the peaks corresponding to an expansion in its wave number range show the weakening of the B-O, B-OH and B-H bonds by the mechanical energy arising from the continuous collisions between the particles and milling balls during the milling.

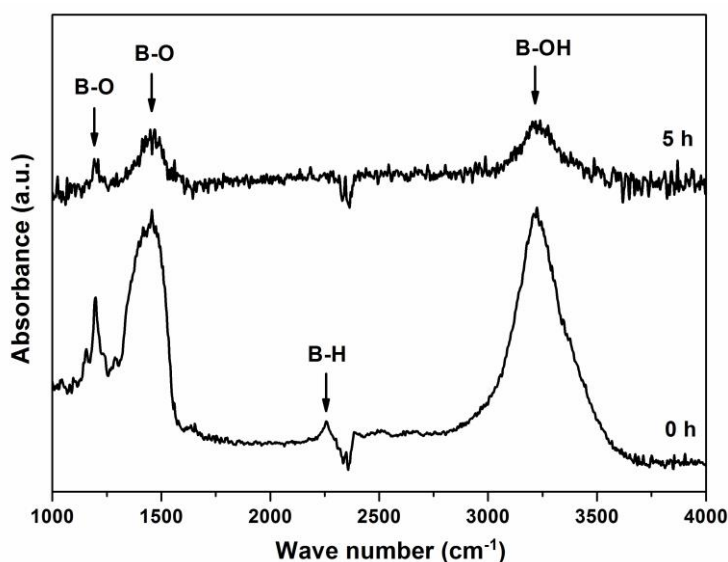
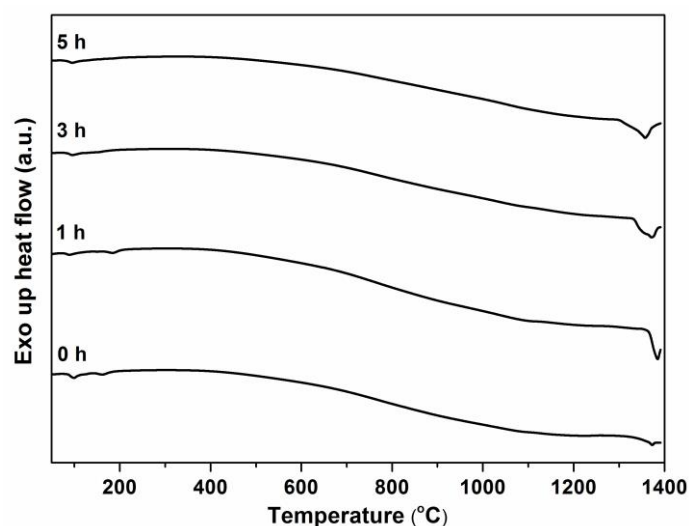


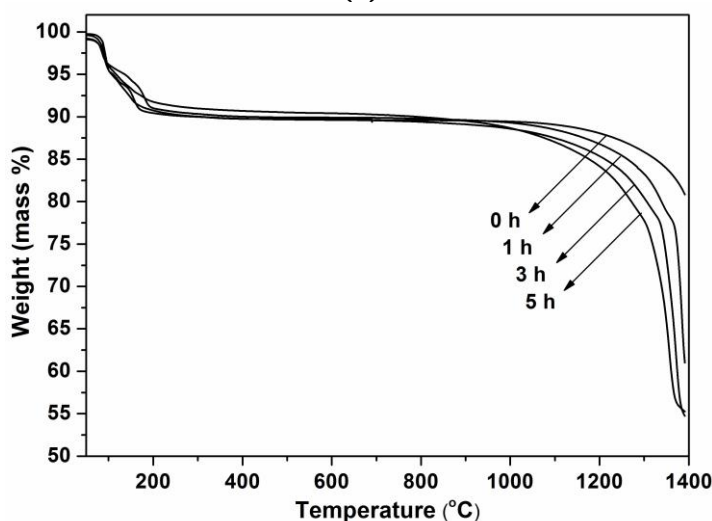
**Figure 4.31** : FTIR spectra of the as-blended  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-C}$  powders and those milled for 5 h.

Figure 4.32(a)-(b) are the DSC and TG scans, respectively, of the as-blended powders and those milled for 1, 3 and 5 h. The DSC scans show small endothermic peaks in the vicinity of 90 and 190 $^{\circ}\text{C}$ , corresponding to the release of humidity and the vaporization of water that is adsorbed to the  $\text{B}_2\text{O}_3$  (Figure 4.31) (Jalaly et al,

2014; Yaghoubi and Torabi, 2014). These endotherms account for a powder weight loss of approximately 10 % up to 200°C (Figure 4.32(b)). These two low-temperature endotherms are also consistent with those in the DSC scans of B<sub>2</sub>O<sub>3</sub>-containing powder blends reported by the previous studies (Jalaly et al, 2014; Yaghoubi and Torabi, 2014). As observed from Figure 4.32(a), no other endothermic or exothermic peaks are present in the DSC scans of all the powders between the temperatures of ~200 and ~1300°C. However, above 1300°C, all powders exhibit distinct endotherms that have different shapes, onset temperatures and peaking points. As-blended powders exhibit a very small endotherm peak at approximately 1374°C, whereas powders milled for 1 h have a sharp endotherm peak at approximately 1386°C. On the other hand, there are broad endotherms having maximum values at approximately 1372 and 1357°C for the 3 and 5 h milled powders, respectively. In addition to the shallow endotherm of the as-blended powders, the onset temperatures of the endotherms in the 1, 3 and 5 h milled powders (respectively approximately 1360, 1320 and 1300°C) decrease as the milling time increases from 1 to 5 h. Moreover, the TG scans of the as-blended and milled powders are almost constant in the temperature range between ~200 and ~1000°C (Figure 4.32(b)), but the total weights of the powders decrease after the oven temperature of the calorimeter reaches 1000°C. The total weight losses of the powders upon heating from 200 to 1400°C are 9, 29, 35 and 36 % for 0, 1, 3 and 5 h, respectively, as observed in Figure 4.32(b). Thus, the weight losses of the powders become larger as the milling time increases. To determine the different endothermic behaviours of the as-blended and milled powders containing Nb<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub> and C phases (Figure 4.30), XRD analyses were carried out on the specimens subjected to DSC analysis.



(a)



(b)

**Figure 4.32 :** DSC-TG analyses of the as-blended  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-C}$  powders and those milled for 1, 3 and 5 h: (a) DSC scans and (b) TG scans.

Figure 4.33 shows the XRD patterns of the DSC samples (heated up to  $1400^\circ\text{C}$ ) of the as-blended powders and those milled for 5 h. The XRD pattern of the as-blended powders shows a high amount of  $\text{NbO}_2$  (ICDD Card No: 019-0859, Bravais lattice: primitive monoclinic,  $a=1.203$ ,  $b=1.437$ ,  $c=1.036$  nm) and a reduced amount of C phases in the presence of fewer  $\text{NbC}$  (ICDD Card No: 071-070-8416, Bravais lattice: face-centred cubic,  $a=b=c=0.447$  nm) and  $\text{Nb}_2\text{O}_5$  phases, whereas the XRD pattern of the 5 h milled powders shows a high amount of  $\text{NbC}$  phase with a very low amount of C and  $\text{Nb}_2\text{O}_5$  phases. Although there is no sign of  $\text{B}_2\text{O}_3$  melting at approximately  $450^\circ\text{C}$  in the DSC scans in Figure 4.32(a), the XRD patterns in Figure 4.33 do not display any boron-related products after heating both the as-blended and 5 h of milled powders. This might be due to much lower intensities of  $\text{B}_2\text{O}_3$  than of the

$\text{Nb}_2\text{O}_5$ ,  $\text{NbO}_2$ ,  $\text{NbC}$  and  $\text{C}$  phases. The results of phase analyses of the DSC samples will be evaluated along with those of the annealed powders to reveal the reaction mechanism, in the “The effect of milling and annealing on the reaction mechanism” section.

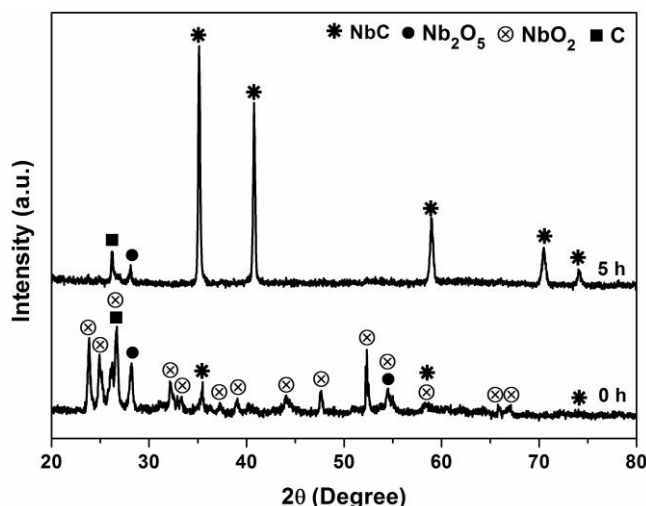
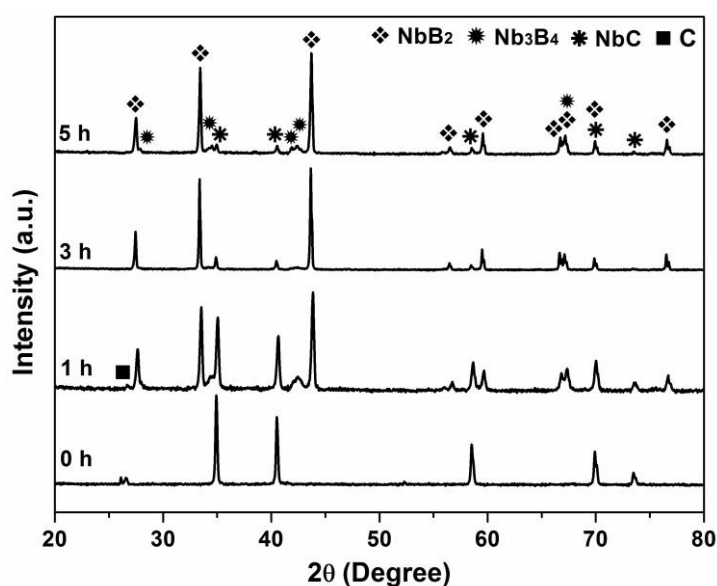


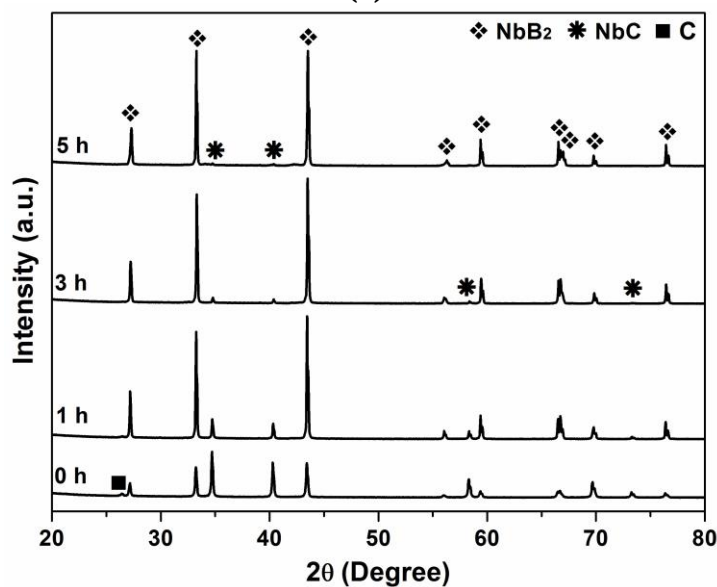
**Figure 4.33 :** XRD patterns of the DSC samples (heated up to 1400 °C) of the as-blended powders and those milled for 5 h.

Figure 4.34(a)-(b) illustrate the XRD patterns of the as-blended and milled (for 1, 3 and 5 h) powders after annealing at 1300 and 1400°C for 12 h, respectively. Although the XRD patterns of the DSC sample in the as-blended condition revealed  $\text{NbO}_2$  and  $\text{C}$  as the dominant phases (Figure 4.33), the  $\text{NbC}$  phase with a small amount of unreacted  $\text{C}$  is obtained in the as-blended powders after annealing at 1300°C for 12 h (Figure 4.34(a)). After milling for 1 h and annealing at 1300°C for 12 h,  $\text{NbB}_2$  (ICDD Card No: 35-0742, Bravais lattice: primitive hexagonal,  $a=b=0.3111$  nm,  $c=0.327$  nm),  $\text{Nb}_3\text{B}_4$  (ICDD Card No: 03-065-2553, Bravais lattice: body-centred orthorhombic,  $a=0.330$  nm,  $b=1.408$  nm,  $c=0.314$  nm) and  $\text{NbC}$  with the presence of  $\text{C}$  were observed in the XRD patterns (Figure 4.34(a)). X-ray reflections for the  $\text{NbB}_2$  phase contain 9 peaks at values of  $2\theta=27.214^\circ$ ,  $33.233^\circ$ ,  $43.455^\circ$ ,  $56.155^\circ$ ,  $59.374^\circ$ ,  $66.486^\circ$ ,  $66.796^\circ$ ,  $69.750^\circ$  and  $76.380^\circ$ , which are indexed as the  $\{001\}$ ,  $\{100\}$ ,  $\{101\}$ ,  $\{002\}$ ,  $\{110\}$ ,  $\{111\}$ ,  $\{102\}$ ,  $\{200\}$  and  $\{201\}$  families of planes, respectively. As the milling time increases from 1 to 5 h, the intensity of the  $\text{NbC}$  phase significantly decreases. A small amount of the  $\text{Nb}_3\text{B}_4$  phase still remains in the structure even after milling for 5 h and subsequent annealing at 1300°C (Figure 4.34(a)). The simultaneous formation of the  $\text{NbB}_2$  and

$\text{Nb}_3\text{B}_4$  phases could also be expected in light of the Nb-B binary phase diagram where the  $\text{NbB}_2$  and  $\text{Nb}_3\text{B}_4$  phases were defined as stable compounds having approximate melting points of 2980 and 2700°C, respectively (Massalski, 1990). However, after annealing at 1400°C for 12 h, the  $\text{Nb}_3\text{B}_4$  phase completely disappears in the XRD patterns of all the milled powders (Figure 4.34(b)), emphasising the effect of annealing temperature on the phase transformation of niobium borides. Furthermore, there are no additional compounds between C-B, C-B-O, Nb-B-O, Nb-B-C, etc. that can be detected by the XRD analyses of the milled and annealed powders given in Figure 4.34(a) and (b).



(a)



(b)

**Figure 4.34 :** XRD patterns of the as-blended, milled and annealed powders: (a) after annealing at 1300°C for 12 h and (b) after annealing at 1400°C for 12 h.

Table 4.4 lists the semi-quantitative phase analyses of the as-blended, milled (1, 3 and 5 h) and annealed (1300 and 1400°C) powders obtained from the Rietveld refinement method based on the XRD patterns in Figure 4.34(a) and (b). Increasing the annealing temperature from 1300 to 1400°C resulted in the formation of NbB<sub>2</sub> in the as-blended powders and an increase in the amount of NbB<sub>2</sub> and a decrease in the amount of NbC at constant milling times for all milled powders. Similarly, at a constant annealing temperature (1300 or 1400°C), extending the milling time from 1 to 5 h significantly increases the amount of NbB<sub>2</sub> and decreases the amount of NbC. The highest amount of NbB<sub>2</sub> was obtained from the powders milled for 5 h and annealed at 1400°C for 12 h, which have NbB<sub>2</sub> and NbC phases with amounts of 98.0 and 2.0 wt.%, respectively. The amount of unreacted C decreases with an increase in both milling time (from 0 to 1 h) and annealing temperature. Although no C was detected in the XRD patterns of the powders after milling for 3 and 5 h and annealing at 1300 and 1400°C, this cannot be taken as proof of its absence in these samples due to its low amount, which is less than the detection limit of XRD.

**Table 4.4 :** Semi-quantitative phase analyses of the as-blended, milled (1, 3 and 5 h) and annealed (1300 and 1400°C) powders obtained from the Rietveld refinement method based on their XRD patterns.

| <b>Milling Time (h)</b> | <b>Annealing Temperature (°C)</b> | <b>NbB<sub>2</sub> (wt.%)</b> | <b>NbC (wt.%)</b> | <b>Nb<sub>3</sub>B<sub>4</sub> (wt.%)</b> | <b>C (wt.%)</b> |
|-------------------------|-----------------------------------|-------------------------------|-------------------|-------------------------------------------|-----------------|
| 0                       | 1300                              | -                             | 92.9              | -                                         | 7.1             |
| 1                       |                                   | 49.1                          | 40.1              | 6.2                                       | 4.6             |
| 3                       |                                   | 82.3                          | 14.5              | 3.2                                       | -               |
| 5                       |                                   | 87.5                          | 8.1               | 4.4                                       | -               |
| 0                       | 1400                              | 25.6                          | 70.4              | -                                         | 4.0             |
| 1                       |                                   | 67.9                          | 30.0              | -                                         | 2.1             |
| 3                       |                                   | 89.7                          | 10.3              | -                                         | -               |
| 5                       |                                   | 98.0                          | 2.0               | -                                         | -               |

To reveal the residual C content in the final samples, powders milled for 3 and 5 h and annealed at 1400°C were oxidised at 800°C for 15 min. Based on the weight losses in the final powders after oxidation at 800°C, the free C contents were calculated as approximately 1.0 and 0.4 wt.% of the overall powders milled for 3 and 5 h, respectively, and annealed at 1400°C. This significant elimination of residual C from the final powders without any post-treatment process seems to be essential for further sintering processes because free C in NbB<sub>2</sub>/NbC composites leads to a considerable increase in both the pores and pore sizes and a decrease in the

mechanical properties (Tsuchida and Kakuta, 2006). In a related study, mechanical activation assisted SHS of NbC and NbB<sub>2</sub> was achieved after milling for 60 min and self-ignition; however, a large amount of the Nb phase still remained in the structure (Tsuchida and Kakuta, 2005). In the same study, isothermal heating of the Nb, B and C-containing powder mixtures at 1000 and 1200°C resulted in the formation of NbB<sub>2</sub> and NbB<sub>2</sub>-NbC while leaving considerable amounts of unreacted Nb and C (Tsuchida and Kakuta, 2005).

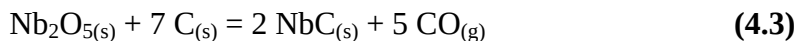
#### **4.3.1 The effect of milling and annealing on the reaction mechanism**

The experimental results showed that milling process has a significant effect on the reaction mechanism of the Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-C system. XRD analyses of the milled powders (Figure 4.30) revealed a significant crystallite refinement and increase in the lattice strains (Table 4.3) which promotes the existence of highly activated C particles in the milled powders (Suryanarayana, 2001). Phase composition differences between the DSC samples (heated up to 1400°C) of the as-blended powders and those milled for 5 h (Figure 4.33) also revealed the emergence of more reactive particles produced by mechanical milling: Due to the higher reactivity of the particles in the 5 h milled powders, the Nb<sub>2</sub>O<sub>5</sub> and C directly convert into the NbC phase without the formation of NbO<sub>2</sub>, leaving behind a very small amount of unreacted Nb<sub>2</sub>O<sub>5</sub> and C particles. On the basis of Figures 4.32 and 4.33, the small endothermic peak at approximately 1374°C in the as-blended powders (Figure 4.32(a)) can be attributed to the formation of two new phases, NbO<sub>2</sub> arising from the reaction between Nb<sub>2</sub>O<sub>5</sub> and C according to reaction (4.1) and NbC arising from the reaction between NbO<sub>2</sub> and C according to reaction (4.2).



On the other hand, a broad endothermic peak with an onset temperature of ~1300°C and a maximum point of ~1357°C is observed in the DSC scans of 5 h milled powders, given in Figure 4.32(a). Because the XRD pattern of the DSC sample milled for 5 h and heated up to 1400°C (Figure 4.33) exhibits Nb<sub>2</sub>O<sub>5</sub> and C peaks with very small intensities and no NbO<sub>2</sub> peaks, it can be stated that the reactions (4.1) and (4.2) take place concurrently in the milled powders. Thus, the sharp and broad endothermic peaks of the milled powders (Figure 4.32(a)) emerge as a consequence

of the NbC formation arising from the total reaction between Nb<sub>2</sub>O<sub>5</sub> and C as per reaction (4.3).



Thermodynamic enthalpy change values ( $\Delta H_T$ ) at the endothermic peak temperatures of the as-blended and 5 h of milled powders for the predicted reactions (4.1), (4.2) and (4.3) are  $\Delta H_{1374^\circ\text{C}} = 207.7 \text{ kJ/mol}$ ,  $\Delta H_{1374^\circ\text{C}} = 398.1 \text{ kJ/mol}$  and  $\Delta H_{1357^\circ\text{C}} = 1004.9 \text{ kJ/mol}$ , respectively. These values justify the significant heat difference between the small endotherm of the as-blended and the sharp endotherm of the 5 h milled powders (Figure 4.32(a)).

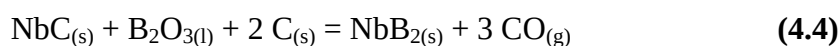
Moreover, the weight losses confirmed by DSC/TG analyses (upon heating from 200 to 1400°C) also support the fact that a carbothermal reaction occurred, resulting in CO gas emission (Figure 4.32(b)). As the milling time is prolonged and hence the powder particles have a high and active surface area indicating high reactivity, the concurrent reactions (4.1) and (4.2) increase the formation of NbC and the amount of gaseous product. A significant increase in the CO gas emission after 5 h of milling could also be expected as the amount of CO<sub>(g)</sub> in the reaction (4.3) is considered. These weight losses corresponding to the CO gas emissions are in good agreement both with the reaction products characterised by the XRD and DSC analyses and the predicted reaction mechanism in reactions (4.1)-(4.3). Consequently, DSC scans (Figure 4.32(a)) and subsequent XRD analyses (Figure 4.33) showed that milling contributes to the formation of NbC. Comparing the DSC scans of the 1 and 5 h milled powders, it can be clearly observed that the formation temperature of the NbC phase decreases by approximately 29°C upon the 4 h of additional milling (Figure 4.32(a)).

Although the thermodynamic prediction in Figure 3.6 indicated that the Nb<sub>2</sub>O<sub>5</sub> completely disappears at 1000°C, the NbC appears at 1000°C and remains stable up to 1400°C with its maximum molar quantity in the presence of liquid B<sub>2</sub>O<sub>3</sub>. The DSC sample of the as-blended powders heated up to 1400°C in Figure 4.33 includes unreacted Nb<sub>2</sub>O<sub>5</sub>, a small amount of NbC and NbO<sub>2</sub> in addition to the unreacted C. Moreover, the amount of C consumption and hence the amount of CO gas emission are almost constant between the temperatures of 1000 and 1400°C according to the thermodynamical calculation in Figure 3.6. However, the TG scan of the as-blended

sample in Figure 4.32(b) shows a decrease in the total weight of the heated powders, originating from the reduction of Nb<sub>2</sub>O<sub>5</sub> to NbO<sub>2</sub> and the formation of NbC. Further, the emergence of the NbB<sub>2</sub> phase at 1400°C with the decreasing amounts of liquid B<sub>2</sub>O<sub>3</sub> and NbC (Figure 3.6) could not be observed in the DSC sample of as-blended powders (Figure 4.33). These phenomena can be attributed to the non-isothermal fast DSC heating conditions carried out in an alumina crucible in which particles of the raw materials react with each other in a very small volume. Because the results of the thermodynamic calculations show only the equilibrium phase composition at room temperature without considering the unsteady state conditions of the reaction kinetics, it is expected that the outputs of the FactSage<sup>TM</sup> data and the DSC experiments will differ from each other. The objective of the FactSage<sup>TM</sup> calculation is to predict thermodynamic (equilibrium) product phases. Because the thermodynamic data are for only equilibrium conditions that do not take into account the synthesis history and far-from-equilibrium mechanical milling parameters, comparison of the reaction products of the milled and heated powders with the predicted values is not appropriate.

On the other hand, the phase composition of the as-blended powders after annealing at 1300°C for 12 h (Figure 4.34(a)) is in good agreement with the thermodynamic prediction given in Figure 3.6: The maximum formation of NbC was expected after heating at 1000°C in the presence of unreacted C and effluent gaseous product and in which there is no evidence of NbB<sub>2</sub> formation under the temperature of 1400°C. The coherence of the results obtained from the FactSage<sup>TM</sup> data and the annealing (1300°C for 12 h) experiments as opposed to those from the DSC analysis are because of the time factor during annealing. Because of the long annealing time (12 h), all of the resultant phases predicted by FactSage<sup>TM</sup> formed after annealing at 1300°C. This was not the case for the DSC experiments due to the non-isothermal heating conditions and the lack of a holding time prior to the XRD investigations. It seems that all NbO<sub>2</sub> and unreacted Nb<sub>2</sub>O<sub>5</sub> transforms to NbC due to the effect of the 12 h holding time at 1300°C, based on the reaction (4.2).

After annealing at 1300°C for 12 h as the steady state conditions are attained during the holding time, NbC reacts with B<sub>2</sub>O<sub>3</sub> and the remaining C, in accordance with the reaction (4.4).



The formation of  $\text{NbB}_2$  in the milled powders was achieved by means of the 12 h holding time during annealing because no peaks corresponding to its presence were observed in the DSC scans (Figure 4.32(a)). Moreover, the reduced formation temperature of the NbC phase upon increasing the milling time, as already exhibited in the DSC scans in Figure 4.32(a), corresponds to a reduction in the  $\text{NbB}_2$  formation temperature at the same time, based on the reaction (4.4). Although the onset formation temperature of  $\text{NbB}_2$  was reported as  $1400^\circ\text{C}$  for the thermodynamical calculations of  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-C}$  system given in Figure 3.6, XRD results revealed that the formation temperature of  $\text{NbB}_2$  was decreased by means of the milling process before annealing.

The selection of a relatively longer milling time than that of a conventional mechanical activation process contributes positively to the reaction mechanism, which commonly requires temperatures higher than  $1400^\circ\text{C}$  for the nearly complete conversion of the reactants. A study in the current literature reports the reaction mechanism of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-C}$  system and claimed that the overall carbothermal reduction reaction (3.5) proceeded through the reactions (4.1), (4.2) and (4.4), indicating the formations of  $\text{NbO}_2$ , NbC and  $\text{NbB}_2$  (Maeda, 1994). Similarly, the carbothermal reduction of  $\text{TiO}_2$  to  $\text{TiB}_2$  proceeded in two steps through  $\text{Ti}_3\text{O}_5$  and TiC (Kang and Kim, 2007). These mechanisms are compatible with the proposed mechanism of the carbothermal process in this study for the annealed powders prepared without milling. However, when the powder blends are milled, the carbothermal process does not include the reaction steps (4.1) and (4.2) separately but rather includes them concurrently because  $\text{Nb}_2\text{O}_5$  directly reacted with the highly activated C powders (as provided by the crystallite refinement shown in Table 4.3) to form NbC according to reaction (4.3) (Suryanarayana, 2001; Tsuchida and Kakuta, 2005; Yaghoubi and Torabi, 2014).

Thus, the occurrence of two reactions in one step, which affects the rate of the overall reaction (3.5), can be taken as an explanation of the reduced reaction temperatures during annealing for the milled powders (Kang and Kim, 2007). Consequently, the reaction mechanism of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-C}$  system, the onset and peak reaction temperatures and the types and amounts of the products are highly affected by the milling process due to the mechanical activation of the raw materials

during the repeated fracturing and welding of powder particles (Suryanarayana, 2001).

#### **4.3.2 Microstructure of the milled and annealed powders**

Figure 4.35(a)-(c) display the secondary electron SEM images of the as-blended, milled (for 5 h) and annealed (at 1400°C) powders. As observed from Figure 4.35(a), as-blended powders have irregular agglomerates presenting a heterogeneous morphology of Nb<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub> and C particles. The small, white particles in Figure 4.35(a) are B<sub>2</sub>O<sub>3</sub> particles partially dissolved in ethanol during sample preparation. After milling for 5 h, the particles have much closer contact points and a uniform distribution, as shown in Figure 4.35(b), compared to those of as-blended powders in Figure 4.35(a), indicating the effect of mechanical milling throughout the microstructure. The SEM image of the 5 h milled powders in Figure 4.35(b) presents rounded-shaped particles embedded in irregular agglomerates with sizes below 2 µm. It can be said that the discrete appearance of the Nb<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub> and C particles disappears after 5 h of milling by both the contribution of the milling process and the lubricating effect of the graphite particles.

The microstructure of the powders after milling for 5 h and annealing at 1400°C in Figure 4.35(c) clearly exhibits the formation of particles having irregular shapes ranging in sizes between 500 nm and 3.5 µm. This supports the formation of new phases (Figure 4.34(b)) and reveals the effect of annealing at 1400°C for 12 h by changing the morphologies of the particles.

In contrast to the porous and agglomerated microstructure of combustion-synthesised niobium boride powders, carbothermal products consist of distinct powder particles with clear boundaries (Maeda, 1994; Takeya et al, 2004; Kang and Kim, 2007; Yeh and Wang, 2010; Qiu et al, 2012). The effect of annealing can be observed in some coalesced particles that were partially sintered (Figure 4.35(c)).

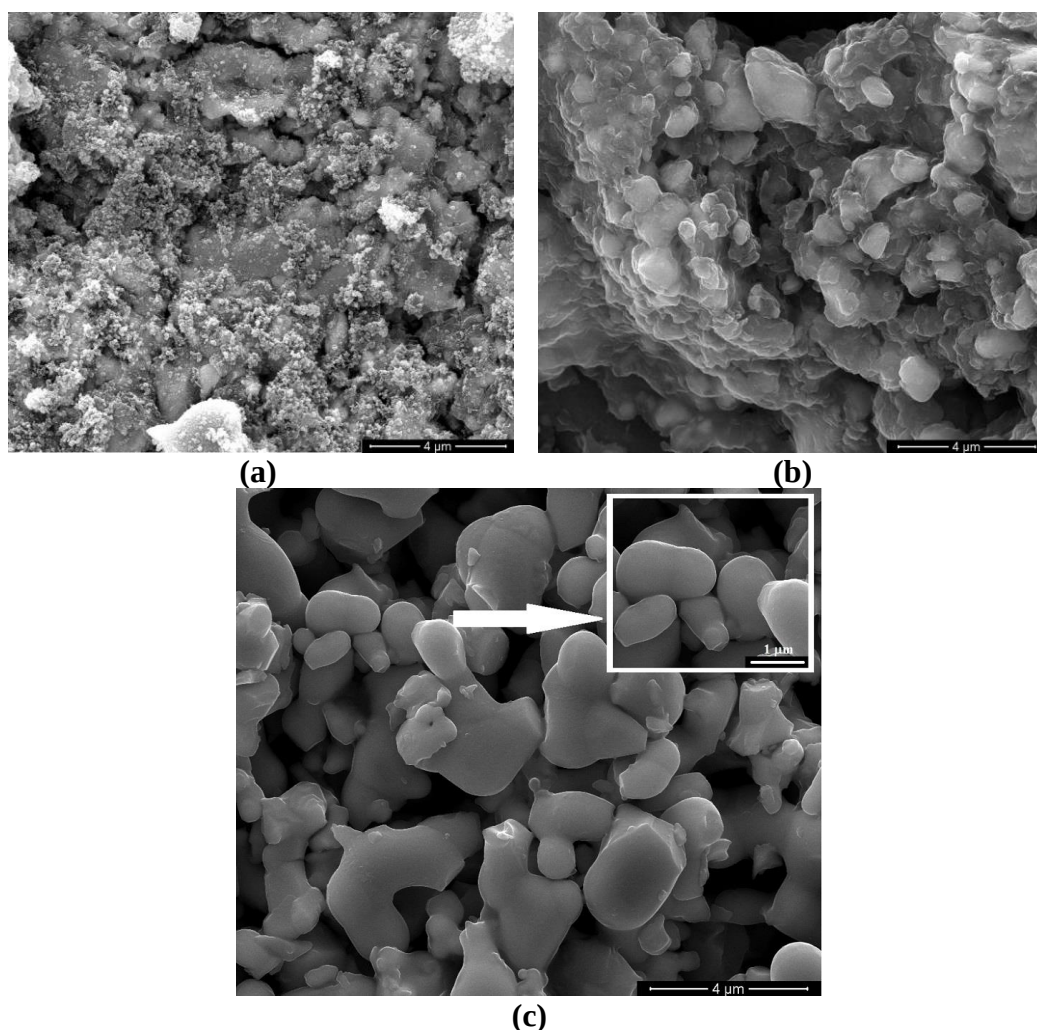


**Figure 4.35 :** SEM images of the as-blended, milled and annealed powders: (a) as-blended, (b) milled for 5 h and (c) milled for 5 h and annealed at 1400°C.

To reveal the phase distribution after milling for 5 h, SEM/EDX analysis was carried out on compacted pellets of the 5 h milled powders. Figure 4.36(a)-(b) present the secondary electron SEM image and the associated elemental maps, respectively, for B, C and Nb taken from the pellet of the 5 h milled powders. The O elemental map is not included in Figure 4.36(b) due to the observation complexity of the signals arising from other elements. Even so, elemental O is distributed uniformly throughout the microstructure.

The elemental mapping of the 5 h milled powders is compatible with their XRD pattern in Figure 4.30 and FTIR spectra in Figure 4.31, which revealed the existence of  $\text{Nb}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$  and C. Thus, Figure 4.36(b) verifies the uniform distribution of the raw materials and the intimate contact between the activated particles throughout the microstructure. A similar observation was reported for the particles obtained by the

milling of Nb, B and C containing powder mixtures, and it was stated that the initial sizes of the Nb particles decreased and they were covered completely with the fine particles of C and B (Tsuchida and Kakuta, 2005).

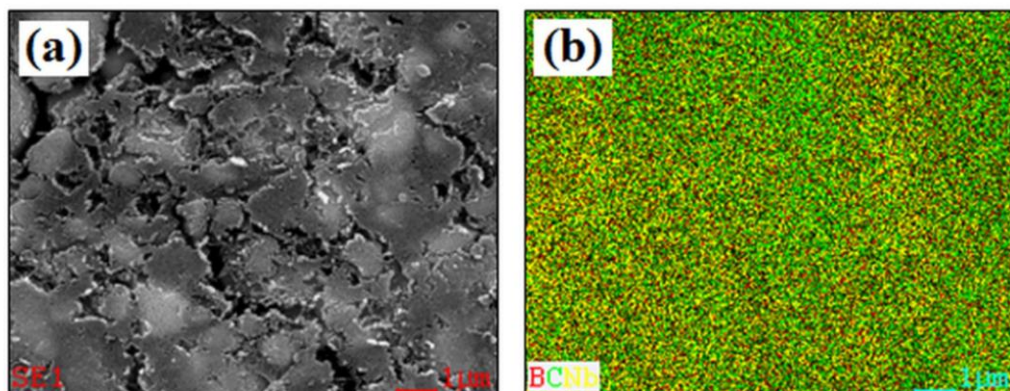


**Figure 4.36 :** SEM/EDX analysis of the pellet obtained from the compaction of the 5 h milled powders: (a) SEM image and (b) elemental maps for B, C and Nb.

Figure 4.37(a) shows the secondary electron SEM image, and Figure 4.37(b)-(d) illustrate the associated elemental maps (Nb, B and C) taken from the powders milled for 5 h and annealed at 1400°C. Nb, B and C elemental maps clearly indicate the presence of these elements throughout the microstructure. The elemental B map (Figure 4.37(c)) coincides almost entirely with the Nb elemental map (Figure 4.37(b)), suggesting the presence of a niobium boride phase. Considering the calculated free C content of 0.4 wt. % for the 5 h milled powders, it can be claimed that the elemental C originated from the NbC phase because the spots on the C map in Figure 4.37(d) overlap with those on the Nb map in Figure 4.37(b). The C elemental map seems to fill the gaps where the B elemental map does not coincide with the Nb elemental map. Thus, the elemental mapping in Figure 4.37(b), (c) and (d) confirms the presence of the NbB<sub>2</sub> and NbC phases and the absence of any intermediate phase or impurity, as observed in the XRD patterns in Figure 4.34(b).

Consequently, the simultaneous formation of NbB<sub>2</sub> and NbC was achieved with a uniform distribution throughout the microstructure after milling for 5 h and annealing at 1400°C (Figure 4.34(b) and Figure 4.37). This is most likely due to the intimate contact between the mechanically activated and uniformly distributed powder particles, as proven by the SEM/EDX analyses of the 5 h milled powders provided in Figure 4.36 and due to their intense carbothermal reduction (Tsuchida and Kakuta,

2005). Moreover, elemental mapping suggests the *in situ* formation of NbB<sub>2</sub>-based composite powders comprising NbC because a single particle contains both phases in the sample volume.

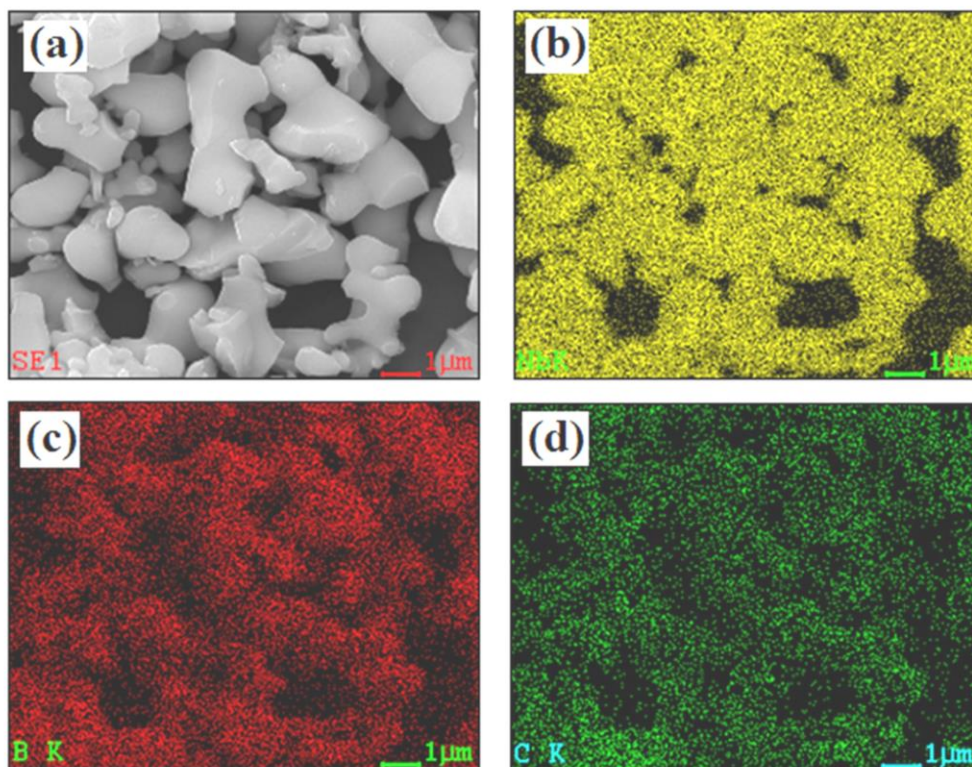


**Figure 4.37 :** SEM/EDX analysis of the powders milled for 5 h and annealed at 1400°C: (a) SEM image, and elemental maps for (b) Nb, (c) B and (d) C.

Figure 4.38(a)-(d) display the bright-field (BF) TEM images and the corresponding selected area diffraction pattern (SADP) taken from powders milled for 5 h and annealed at 1400°C. The neck formation between two particles arising from high temperature can be clearly observed from the encircled area in the TEM image in Figure 4.38(a) showing particle coalescence and hence grain growth observed in the SEM image in Figure 4.35(c). Figure 4.38(b) is a BF image of a spheroidal-shaped particle approximately 600 nm in size. SADP taken from this particle in Figure 4.38(c) is a single crystal spot pattern (Camera length is 80 cm and zone axis is [022]) and verifies the presence of the hexagonal NbB<sub>2</sub> phase, which also conforms well to the dominant phase in the XRD patterns given in Figure 4.34(b). SADP taken from this particle in Figure 4.38(d) is a single crystal spot pattern (Camera length is 80 cm and zone axis is [021]) and also verifies the presence of the hexagonal NbB<sub>2</sub> phase. Additional TEM characterizations carried out on other regions of the grains

shown in Figure 4.38(a) and (b) revealed single crystal spot patterns with different zone axes, all belonging to the NbB<sub>2</sub> phase.

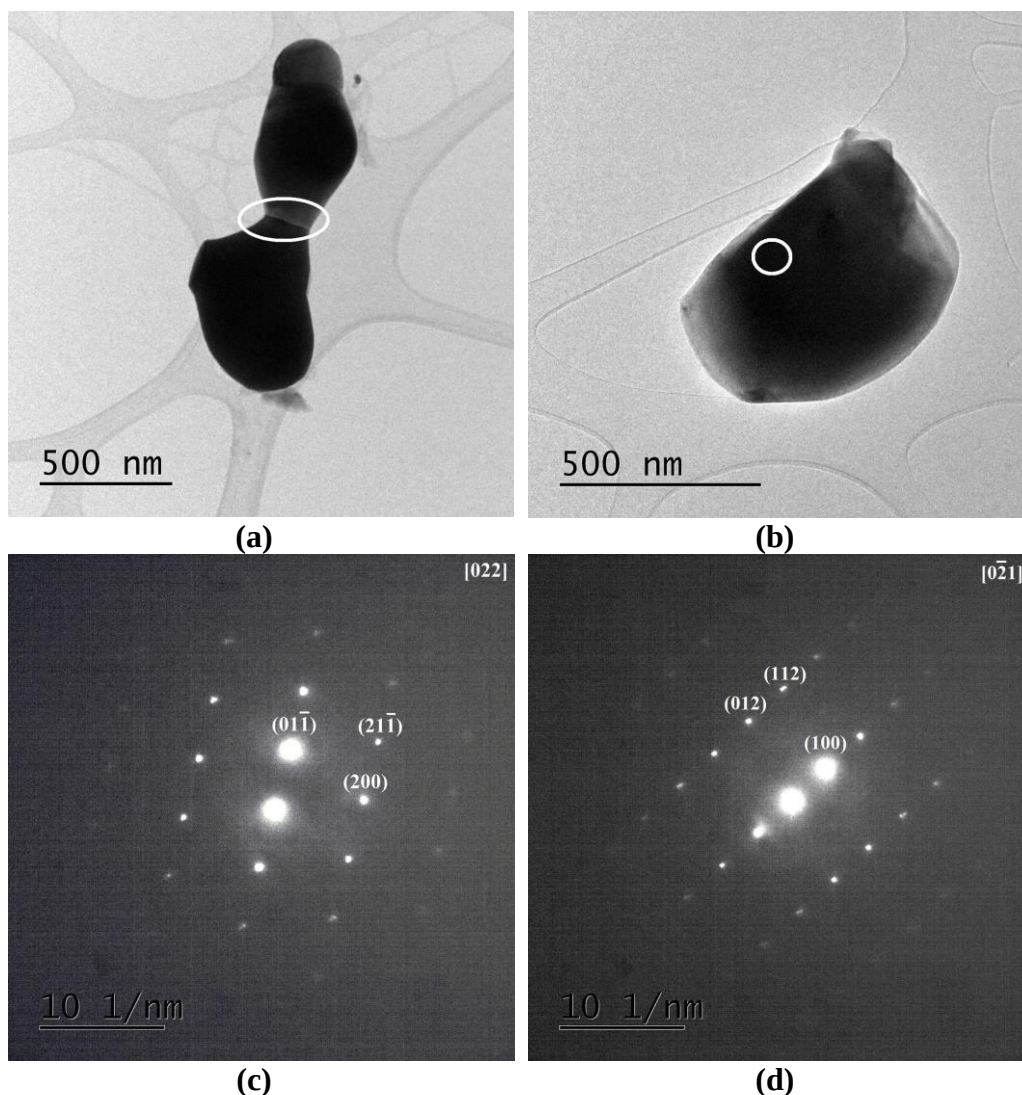


**Figure 4.38 :** TEM images of the powders milled for 5 h and annealed at 1400°C: (a) bright-field (BF) image with encircled area indicating necking, (b) bright-field (BF) image, (c) its corresponding selected area diffraction pattern (SADP) revealing the presence of NbB<sub>2</sub> (Camera length is 80 cm and zone axis is [022]) and (d) its corresponding selected area diffraction pattern (SADP) revealing the presence of NbB<sub>2</sub> (Camera length is 80 cm and zone axis is [021]).

As a conclusion, NbB<sub>2</sub>-based composite powders comprising NbC of approximately 600 nm in size were obtained with high purity from stoichiometric Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-C powder blends milled for 5 h and annealed at 1400°C for 12 h.

Due to the combination of the excellent properties of NbB<sub>2</sub> and NbC, fine and homogeneous microstructures of these ceramics can be a potential precursor powder for the development of NbB<sub>2</sub>-based dense bodies or as a potential reinforcement in

metal matrix composites. Niobium carbide is a refractory ceramic with promising properties such as a high melting point ( $\sim 3600^{\circ}\text{C}$ ), high hardness, excellent chemical stability and good wear resistance (Shi et al, 2005; Ma et al, 2009; Jha and Awana, 2012). Among transition metal carbides, NbC has received great attention due to its applications in the mechanical, chemical and microelectronics industries (Shi et al, 2005). It can find applications in the production of hard materials for reinforcement, in heating elements of electric resistance furnaces and as a catalyst (Ma et al, 2009). The superconductivity of NbC was also reported in some studies (Jha and Awana, 2012). The combined usage of the boride and carbide of niobium in a composite is expected to exhibit improved mechanical properties over their individual forms (Tsuchida and Kakuta, 2005; Tsuchida and Kakuta, 2006). Furthermore, the existence of carbides in the boride matrix drives the formation of a protective layer during oxidation and enhances the oxidation resistance of borides at high temperatures (Gasch et al, 2004). This is significant for high-temperature structural applications of the composites, where oxidation resistance is highly demanded (Gasch et al, 2004).

The application of high temperatures, the use of expensive starting materials and/or the use of complicated equipment to obtain niobium boride may restrict the fabrication process for the desired applications. The preparation of boride-based ceramic powders at a comparatively low temperature without the need for post-synthesis treatment using the carbothermal method may provide a significant improvement in the fabrication process (Kang and Kim, 2007; Balci et al, 2012; Qiu et al, 2012; Hassan et al, 2013). Some limited studies exist in the current literature relating the simultaneous synthesis of NbC and NbB<sub>2</sub> from elemental powder mixtures of Nb, B and C by a mechanical activation-assisted SHS process (Tsuchida and Kakuta, 2005; Tsuchida and Kakuta, 2007). Moreover, it is well known that *in situ* techniques involve chemical reactions that result in the formation of new phases, and this provides a strong matrix reinforcement bond that is not easy to obtain in *ex situ* processes (Gilliard et al, 2014). In this dissertation, a novel and simple solid-state synthesis process is suggested which enables *in situ* formation of NbB<sub>2</sub>-NbC composite powders from oxide starting materials at decreased temperatures due to the effect of mechanical milling.

#### 4.3.3 The effect of excess C on the reaction products and microstructure

The thermodynamical calculations shown in Figure 3.7 exhibited that the maximum values of the reaction products  $\text{NbB}_{2(s)}$  and  $\text{CO}_{(g)}$  can be obtained by a reaction between  $\text{Nb}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$  and C using 100 wt. % stoichiometric excess amount of C. Therefore, additional experiments were carried out by using 100 % stoichiometric excess amount of C in order to show the effects of C content on the reaction products and microstructure.

The XRD patterns of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-C}$  powders milled up to 5 h with 100 wt. % excess of C also revealed the similar results as those milled with stoichiometric C (Figure 4.30), which presented no boride formation after milling for 5 h. Figure 4.39 shows the DSC scans of the as-blended  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-C}$  powders with 100 wt. % excess of C and those milled for 1, 3 and 5 h. As observed from Figure 4.39, no endothermic or exothermic peaks are present in the DSC scans of the as-blended powders, indicating that there is no reaction between  $\text{Nb}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$  and C powders during non-isothermal fast heating conditions of DSC analysis up to  $1400^\circ\text{C}$ . On the other hand, above  $1200^\circ\text{C}$ , all milled powders exhibit distinct endotherms that have different shapes, onset temperatures and peaking points. The powders milled for 1 and 3 h have sharp endotherm peaks at approximately  $1347^\circ\text{C}$  and  $1322^\circ\text{C}$ , respectively. The powders milled for 5 h, however, exhibit a broad endotherm peak having a maximum value at approximately  $1254^\circ\text{C}$ . The endotherm peaks observed in the DSC scans given in Figure 4.32(a) has been attributed to the formation of NbC, during the explanation of the reaction mechanism of  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-C}$  system. The similar phenomenon is also valid for the powders milled with 100 % excess of C, however, the formation temperature of the NbC phase are lower than those of the powders milled with stoichiometric C. As the DSC scans of the powders milled for 5 h without or with the excess amount of C compare to each other, the formation temperature of the NbC phase significantly decreased from  $1357^\circ\text{C}$  to  $1254^\circ\text{C}$  (Figure 4.32(a) and Figure 4.39). Furthermore, comparing the DSC scans of the 1 and 5 h milled powders in Figure 4.39, it can be clearly observed that the formation temperature of the NbC phase decreases by approximately  $93^\circ\text{C}$  upon the 4 h of additional milling. These results promote a decline in the formation temperature of niobium boride phase by increasing C content and milling time, based on the previously explained reaction mechanism.

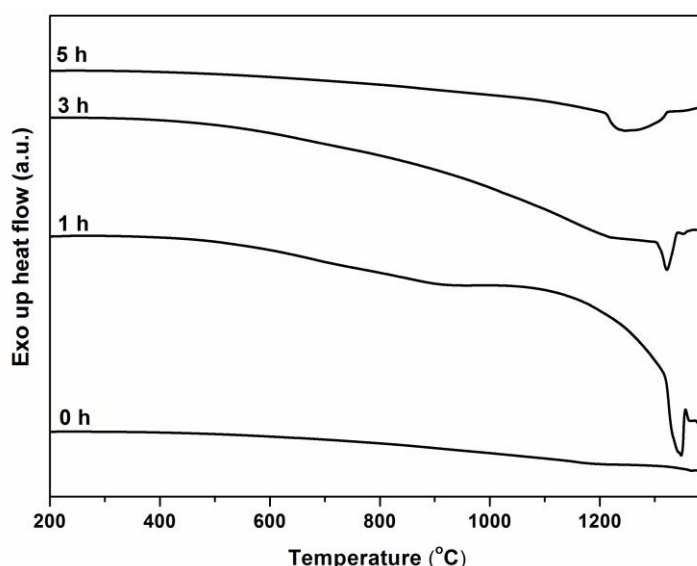
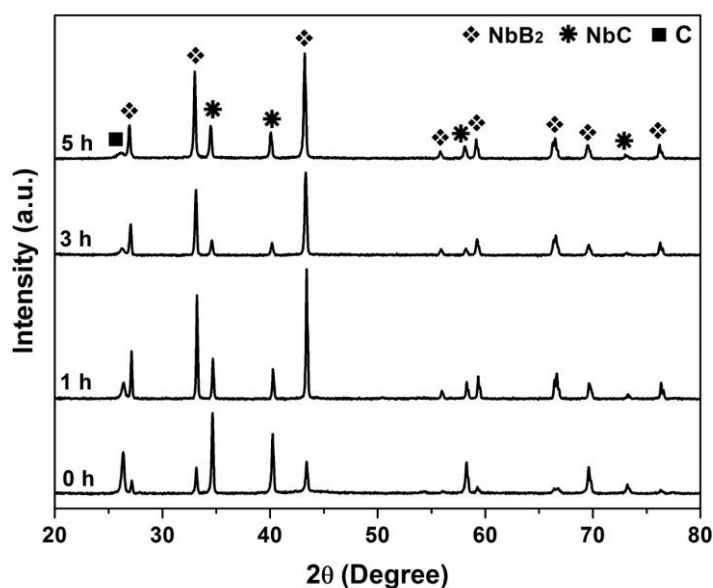
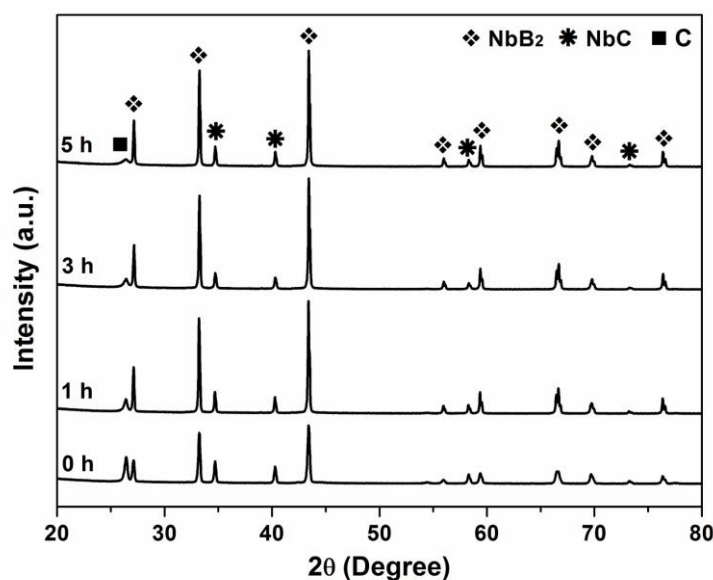


**Figure 4.39 :** DSC scans of the as-blended  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-C}$  powders with 100 wt. % excess of C and those milled for 1, 3 and 5 h.

Figure 4.40(a)-(b) show the XRD patterns of the as-blended  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-C}$  powders with 100 wt. % excess of C, and those milled powders after annealing at 1300 and 1400°C for 12 h. Although the DSC scans of the powders given in Figure 4.39 revealed only the formation of the NbC phase,  $\text{NbB}_2$  and NbC phases are formed after annealing at 1300°C due to the effect of 12 h of holding time (Figure 4.40(a)). However, residual C is observed in the XRD patterns of the as-blended powders and those milled powders after annealing at both 1300 and 1400°C. As seen from Figure 4.40(a)-(b), as the milling time increases from 1 to 5 h, the intensities of C and NbC phases significantly decrease, after annealing at 1300 and 1400°C. The significant contribution of using 100 wt. % excess amount of C on the reaction products is the elimination of  $\text{Nb}_3\text{B}_4$  phase after milling and annealing at 1300°C for 12 h (Figure 4.34(a) and Figure 4.40(a)). It can be concluded that increasing the annealing temperature from 1300 to 1400°C does not significantly affect the reaction products when C is used in 100 wt. % excess amount. Furthermore, the residual C content in the final samples can be easily oxidized at about 800°C and so removed from the powder blends by applying a post-treatment process.



(a)



(b)

**Figure 4.40 :** XRD patterns of the as-blended  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-C}$  powders with 100 wt. % excess of C, and those milled and annealed powders: (a) after annealing at  $1300^\circ\text{C}$  for 12 h and (b) after annealing at  $1400^\circ\text{C}$  for 12 h.

Figure 4.41(a)-(d) demonstrate the secondary electron SEM images of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-C}$  powders with 100 wt. % excess of C milled for 5 h before and after annealing at  $1300^\circ\text{C}$  for 12 h. The SEM image of the 5 h milled powders in Figure 4.41(a)-(b) present rounded-shaped particles embedded in irregular agglomerates with sizes below  $1\ \mu\text{m}$ . The microstructure of the powders after milling for 5 h and annealing at  $1300^\circ\text{C}$  in Figure 4.41(c)-(d) exhibit the formation of porous and agglomerated particles having irregular shapes ranging in sizes between 1 and  $4\ \mu\text{m}$ .

The effect of annealing can be observed in some coalesced particles that were partially sintered (Figure 4.41(d)). The microstructure of the resultant powders prepared with 100 % excess of C is different compared to that of the carbothermal products prepared with stoichiometric C which consists of distinct powder particles (Figure 4.35(c)). This morphology difference can be contributed to the effect of highly-activated C particles and the considerable amount of residual C content in the microstructure of the powders milled for 5 h with 100 wt. % excess of C after annealing at 1300°C.

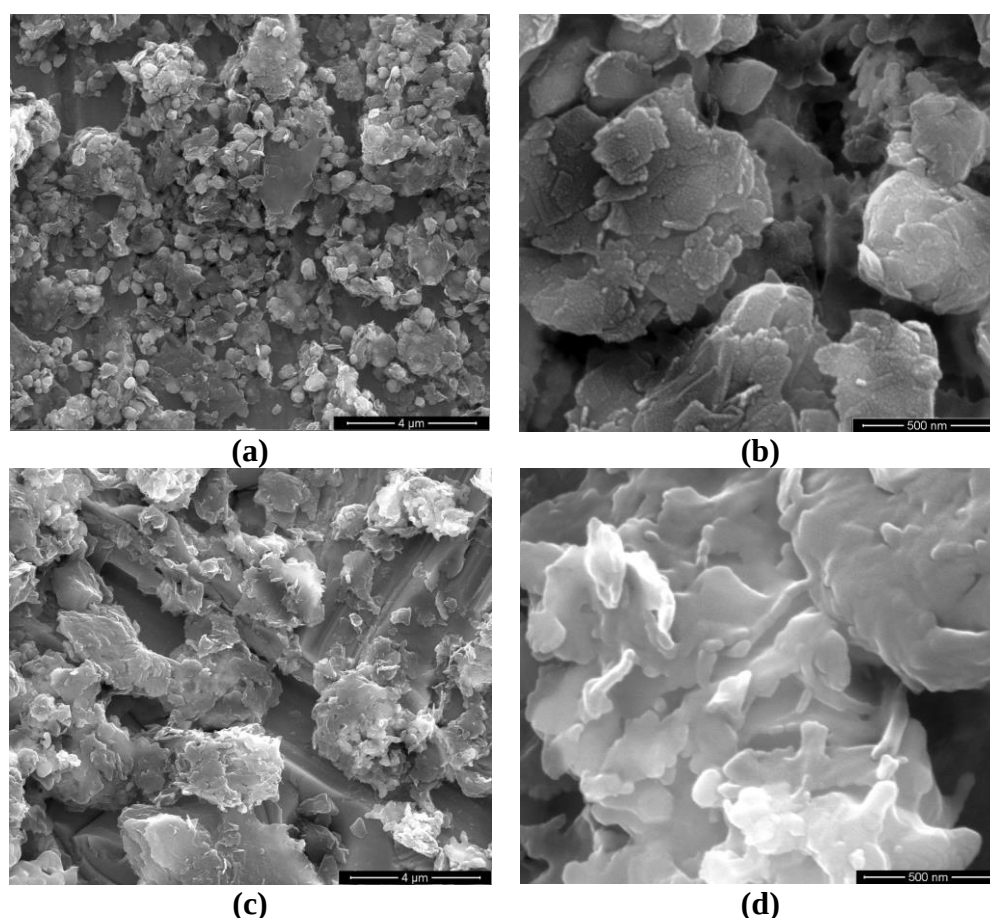


**Figure 4.41 :** SEM images of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-C}$  powders with 100 wt. % excess of C milled for 5 h: (a) before annealing, 20000X, (b) 160000X, (c) after annealing at 1300°C, 20000X and (d) 160000X.

As a conclusion,  $\text{NbB}_2$ -based composite powders comprising NbC ranging in sizes of approximately 1 and 4  $\mu\text{m}$  were obtained with the presence of residual C from  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-C}$  powder blends milled for 5 h with 100 % stoichiometric excess of C and annealed at 1300°C for 12 h. The formation temperature of niobium boride phase decreased by increasing C content and milling time. Furthermore, there were no traces of  $\text{Nb}_3\text{B}_4$  or other non-stoichiometric niobium boride phases. The residual C

content in the final samples could be easily oxidized at about 800°C and so removed from the powder blends by applying a post-treatment process.

#### **4.4 Consolidation and Bulk Properties of the Vanadium and Niobium Borides**

This section includes the microstructural and mechanical characterizations of the sintered vanadium and niobium boride products. The results are discussed regarding the effect of different production conditions and sintering methods on the consolidation behaviour, microstructure and mechanical properties of the bulk samples. Selected powders in high qualities were consolidated by cold pressing/pressureless sintering (PS, with or without Co addition) and spark plasma sintering (SPS) techniques.

Niobium boride powders originated from the mechanochemical reaction of  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  after milling for 5 and 9 h and HCl leaching (Figure 4.18) were consolidated both by PS and SPS techniques without addition (N5-PS, N9-PS, N5-SPS, N9-SPS). Niobium boride powders originated from the mechanochemical reaction of  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  after milling for 5 h and HCl leaching (Figure 4.18) were consolidated by PS using metallic Co sinter additive (2 and 5 wt. % of the total powder amounts) (N5-2CoPS, N5-5CoPS). Vanadium boride powders originated from the mechanochemical reaction of  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  after milling for 7 h with 50 % excess of Mg and HCl leaching (Figure 4.5) were consolidated both by PS and SPS techniques without addition (V7-PS, V7-SPS).

##### **4.4.1 Microstructural characterization and density of the sintered samples**

Figure 4.42(a)-(h) show the OM images of the sintered vanadium and niobium borides consolidated by different conditions and techniques (PS at 1500°C for 4 h, SPS at 1500°C for 15 min). At first sight, it can be obviously seen from the OM images monitored in low magnification that the sinterability of the vanadium and niobium boride samples was improved by changing the sintering conditions and methods from pressureless sintering to activated pressureless sintering and spark plasma sintering. OM images in Figure 4.42(a), (b) and (e) reveal that the sintering conditions (pressureless sintering at 1500°C for 4 h without addition) are inadequate to obtain dense bodies from the high-purity vanadium and niobium boride powders.

Moreover, as the OM images in Figure 4.42(a) and (b) compared to each other, it is evident that mechanical milling for 9 h does not provide any improvement on the microstructures of the niobium boride powders prepared by milling of  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders for 5 h and subsequent leaching. In contrast, the OM image of N9-PS sample exhibits big pores as well as the regional densification. Indentations could not be taken from V7-PS sample because scratch-free mirror surface could not be obtained by typical metallographic treatments. On the other hand, the sintering of the powders at the same conditions with the presence of different amount of Co additive (N5-2CoPS, N5-5CoPS) provides the fine microstructures without any observable pore and segregation in the OM images (Figure 4.42(c) and (d)). It is clearly seen from the OM images in Figure 4.42(c) and (d), the increase in the Co content (from 2 to 5 wt.%) resulted in the cluster formation of secondary phase. This means that densification of niobium boride samples can be feasible at the same temperature with the pressureless sintering, by the use of metallic sintering aid.

Moreover, the size and distribution of the pores in the pressureless sintered samples without aid (N5-PS, N9-PS, V7-PS) decreased substantially in the SPS samples (N5-SPS, N9-SPS, V7-SPS), which indicates the significant contribution of SPS on the densification process. Similar to the pressureless sintering, additional milling of 4 h during powder preparation does not make a significant change on the microstructure of the spark plasma sintered samples (N5-SPS, N9-SPS).

In order to determine the probable contaminations occurred during sintering, bulk products were subjected to the XRD analyses. Based on the XRD analyses, it can be said that there is no contamination or other undesired phases in the microstructures of the bulk samples. As previously given in the XRD patterns (Figure 4.21), single phase NbB formed after annealing at  $1500^\circ\text{C}$  for 4 h of the mechanochemically synthesized niobium boride powders ( $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 5 h and leached with 4 M HCl). Thus, the sintered samples of N5-PS and N9-PS also gave the NbB single phase, as already expected due to the same conditions of the heating treatment. However, SPS of the same powders resulted in a variation on the phase distribution of the bulk samples.

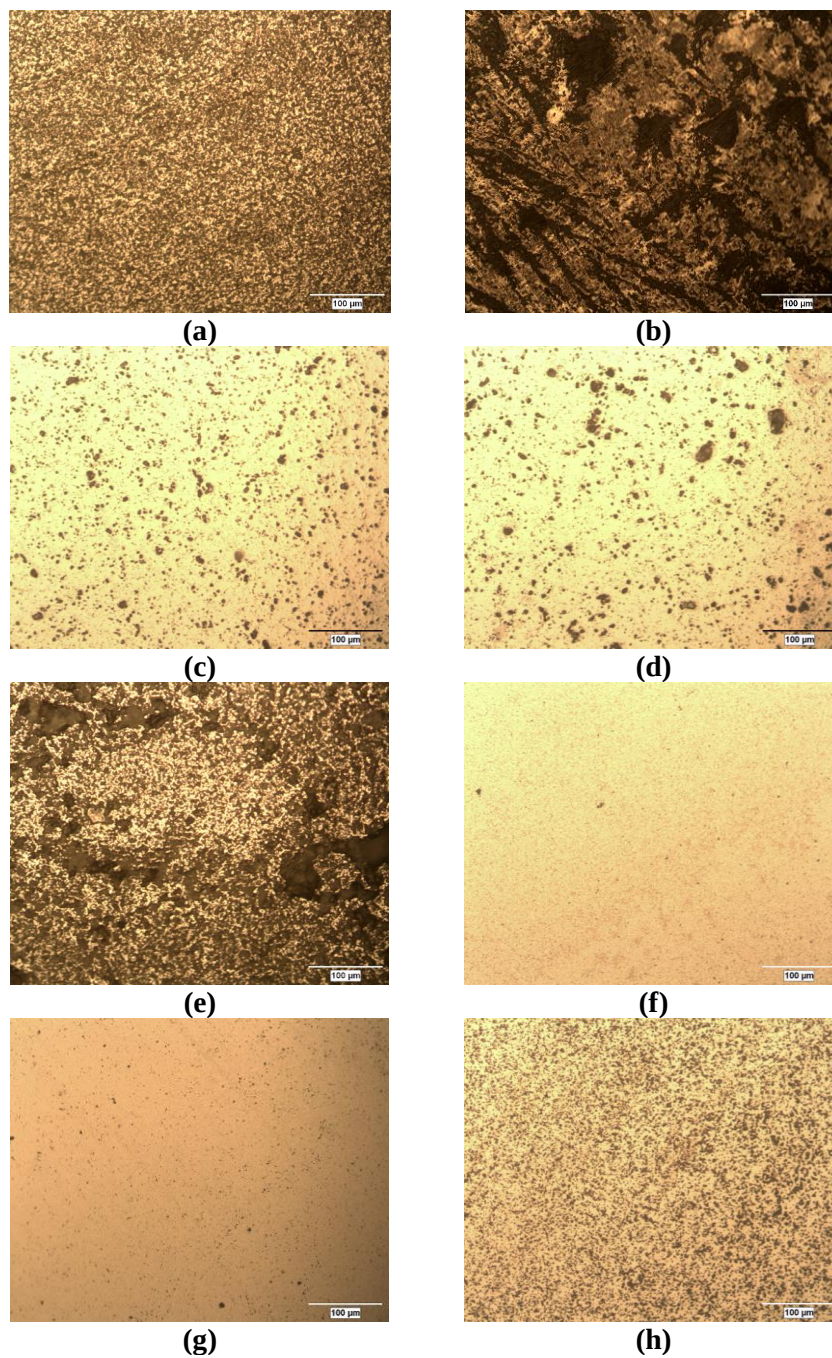


**Figure 4.42 :** OM images of the sintered vanadium and niobium borides:  
 (a) N5-PS, (b) N9-PS, (c) N5-2CoPS, (d) N5-5CoPS, (e) V7-PS, (f) N5-SPS, (g) N9-SPS, and (h) V7-SPS samples.

Figure 4.43 shows the XRD pattern of the spark plasma sintered niobium boride sample (N5-SPS). Unlike the pressureless sintered samples (N5-PS, N9-PS) containing single phase NbB, spark plasma sintered products comprise of dominant NbB phase, with the presence of small amounts of Nb<sub>3</sub>B<sub>4</sub> and Nb<sub>5</sub>B<sub>6</sub> phases. Already, the formation of NbB, NbB<sub>2</sub> and Nb<sub>3</sub>B<sub>4</sub> phases were experienced after powder processing or pressureless sintering. However, the emergence of Nb<sub>5</sub>B<sub>6</sub>

phase is very surprising after SPS since it is an unstable phase with an undefined melting temperature between the stability region of NbB and Nb<sub>3</sub>B<sub>4</sub> phases, in the Nb-B binary phase diagram (Figure 2.5). The non-achievement of the single phase NbB can be attributed to the short holding time (15 min) during SPS which is not sufficient to complete the whole phase transformation. Nevertheless, there is a significant increase in the XRD peaks of NbB after SPS of the synthesized powders, compared with those given in Figure 4.18. This shows the effectiveness of SPS technique which exhibit a local increase in the temperature at the particle contacts due to the applied high electric current through powders. This local temperature rise which significantly enhances the diffusivity of the powders accelerates the phase transformation in a very short time (Sairam et al, 2014).

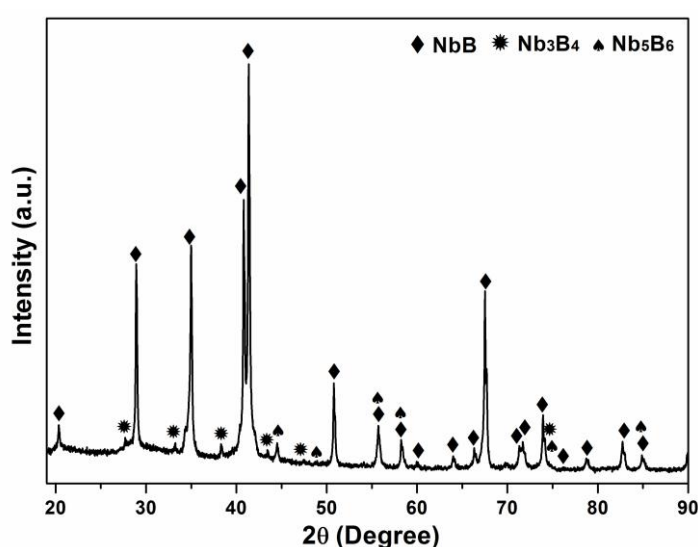


**Figure 4.43 :** XRD pattern of the spark plasma sintered niobium boride sample (N5-SPS).

Figure 4.44 shows the XRD patterns of the pressureless sintered (with the addition of Co) niobium boride samples (N5-2CoPS, N5-5CoPS). As seen from Figure 4.44(a) and (b), Nb<sub>3</sub>B<sub>4</sub> as a dominant phase and a small amount of NbCo<sub>2</sub> (ICDD Card No: 15-0499, Bravais lattice: face-centered cubic, a=b=c= 0.677 nm) intermetallic phase were obtained after cold pressing/pressureless sintering of the mechanochemically synthesized powders (containing NbB-NbB<sub>2</sub>-Nb<sub>3</sub>B<sub>4</sub>) in the presence of 2 and 5 wt. % Co addition. This indicates that a reaction occurred between the dominant phase NbB and Co to form Nb<sub>3</sub>B<sub>4</sub> and NbCo<sub>2</sub> according to the reaction (4.5) during pressureless sintering.



Formation of NbCo<sub>2</sub> arises from the diffusion of Co melt through niobium boride phases and dissolution of them in the liquid Co, at the sintering temperature of 1500°C which is higher than the melting point of Co (T<sub>m</sub>=1495°C). Taking into account of the phase transformation of NbB-NbB<sub>2</sub>-Nb<sub>3</sub>B<sub>4</sub> powders to the single phase NbB at 1500°C for 4 h, it can be claimed that formation of the reaction (4.5) and the transformation of NbB<sub>2</sub> and Nb<sub>3</sub>B<sub>4</sub> phases to NbB phase occur simultaneously during the holding time of sintering. It has been reported in many studies that during pressureless sintering with metallic additives, transition metals (Co, Ni etc.) react with metal borides (TiB<sub>2</sub>, ZrB<sub>2</sub>, etc) to form secondary metallic borides such as Co<sub>2</sub>B, CoB, Ni<sub>2</sub>B, Ni<sub>3</sub>B etc. (Einarsrud et al, 1997; Sanchez et al, 2000; Ağaoğlu et al, 2012). Besides, the formation of these extremely brittle secondary borides has negative effects on the fracture toughness and hardness of the sintered boride samples, especially metallic sintering aid was used over a certain limit (> 10 wt.%) in the total powder blend (Sanchez et al, 2000). On the other hand, there is only one study which reported the formation of Ni<sub>3</sub>Zr intermetallic phase during pressureless sintering of ZrB<sub>2</sub> at 1500°C with 10-50 wt. % Ni additive. The hardness and density of the sintered boride increases with increasing Ni content up to 40 wt. % Ni. It is notable to indicate that the precursor powders used in this study consist of a mixture of stoichiometric and non-stoichiometric zirconium boride phases (ZrB<sub>2</sub>, ZrB and ZrB<sub>15</sub>) (Khanra ve Godkhindi, 2005). As mentioned before, the interaction of single phase metal boride and metallic additive during sintering usually results in the formation of secondary borides. Thus, the reason of the formation of intermetallic phase instead of a secondary boride phase can be attributed to the non-stoichiometric composition of the precursor powders. Furthermore, increasing Co content from 2 to 5 wt. % in the composition causes an increase in the fraction of NbCo<sub>2</sub> phase (Figure 4.44). This means that the diffusion of higher amount of Co into the niobium borides increases the interaction surfaces of the particles, and hence their tendency to yield NbCo<sub>2</sub> phase. Consequently, the unexpected formation of intermetallic phase is considered as an original result in the activated sintering of the metal boride systems.

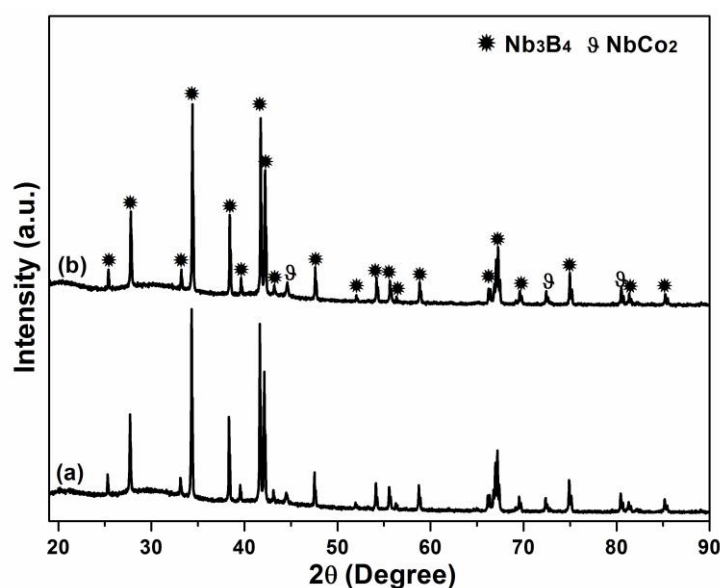


**Figure 4.44 :** XRD patterns of the pressureless sintered (with the addition of Co) niobium borides: (a) N5-2CoPS and (b) N5-5CoPS samples.

In order to show fine microstructures in higher magnification rather than lower magnification screened by OM, back-scattered electron SEM images were taken from the same samples of the niobium and vanadium borides (Figure 4.45(a)-(e)). Figure 4.45(a) does not show a flat surface of a successful sintering process and reveals lots of pores throughout the microstructure whereas the microstructures of the samples in Figure 4.45(b)-(e) have almost no open porosity. On the basis of the XRD patterns given in Figure 4.44(b) and (c) and the working principle of the back-scattered electron (BSE) imaging, the dark particles are assumed to comprise the  $\text{NbCo}_2$  phase. As seen from Figure 4.44(b),  $\text{NbCo}_2$  particles ranging in sizes between 500 nm and 4  $\mu\text{m}$  are uniformly distributed throughout the microstructure. Increasing Co content from 2 to 5 wt. % caused regional agglomerations of the  $\text{NbCo}_2$  particles and formed Co-rich and Nb-rich regions throughout the microstructure (Figure 4.45(c)). Furthermore, the different colour contrasts on the microstructure of the spark plasma sintered niobium boride (N5-SPS) and vanadium boride (V7-SPS) samples are due to the different stoichiometries of the niobium (Figure 4.45(d)) and vanadium boride phases (Figure 4.45(e)). However, the distributed particles of niobium boride phases in different compositions have smaller sizes than those of vanadium borides. The pores in the V7-PS sample are remarkably eliminated and the homogenous microstructure is obtained by SPS of pure vanadium boride powders (V7-SPS).

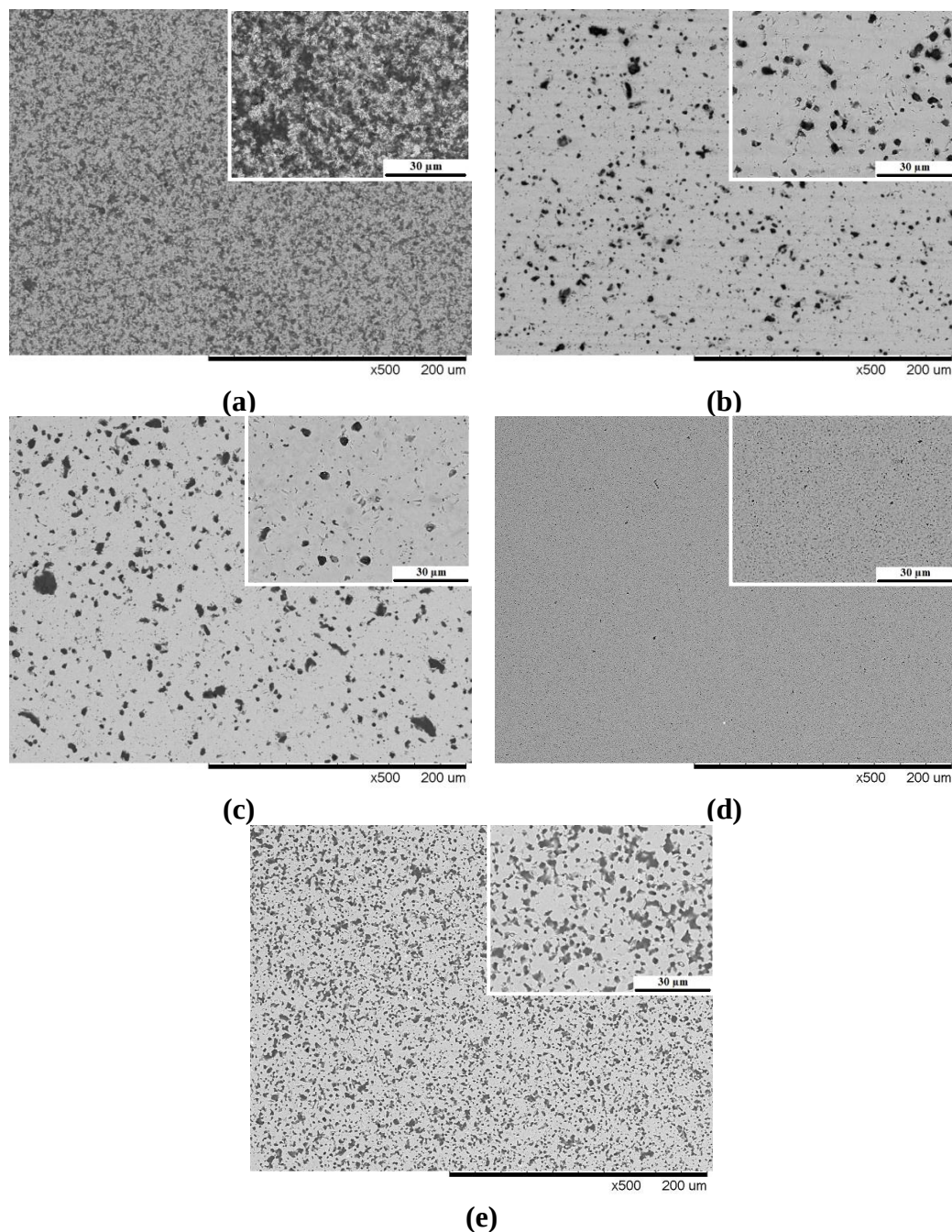


**Figure 4.45 :** SEM/BSE images of the sintered niobium and vanadium borides: (a) N5-PS, (b) N5-2CoPS, (c) N5-5CoPS, (d) N5-SPS and (e) V7-SPS samples.

Theoretical density values of the each sintered sample were recalculated by taking into account of their different phase contents and theoretical, Archimedes and relative densities are given in Table 4.5. Pressureless sintered (N5-PS, N9-PS, V7-PS) samples without any additive exhibit the lowest relative densities ranging in values from about 75 to 82 %. The low relative densities of the sintered products (N5-PS, N9-PS, V7-PS) are due to the insufficient conditions such as low sintering temperature, absence of pressure during sintering or the sinter additive. It has been

reported that in solid-state sintering of the nanoceramics, grain growth/coarsening may dominate the densification process and results in poor density (Golla and Basu, 2014). Moreover, high density values for the sintered pure metal borides are almost impossible to be achieved due to their high melting point and low bulk diffusivity using pressureless sintering (Pastor, 1977; Ağaoğulları et al, 2012). It has been well known that densification can be enhanced with small additions of metallic additives to form the liquid phase (Einarsrud et al, 1997). Thus, the highest relative density was obtained as 97.61 % in the sintered N5-5CoPS sample. The high relative densities (93.74 and 97.61 %) of the N5-2CoPS and N5-5CoPS samples are due to the effect of liquid-phase sintering by means of Co addition. The relative density of the sintered sample with 5 wt. % Co addition increases by about 4 % from the sample containing 2 wt. % Co, indicating that a liquid phase and increase in its amount can improve the densification by higher wetting rate of the boride and Co particles. On the other hand, the relative densities increase as SPS is used instead of pressureless sintering without aid: The relative density of V7-PS sample considerably increases from 82.19 to 90.22 %. This high densification in a very short time (15 min) during SPS can be explained by the applied mechanical pressure (60 MPa) which keeps the powder particles in larger contact during sintering and by means of high-intensity pulsed direct current passing through the powder compacts (Sairam et al, 2014). However, a maximum relative density of 89.45 % is reached by SPS of niobium boride powders (N9-SPS) at 1500°C for 15 min. Sairam et al (2014) reported that the SPS of NbB<sub>2</sub> powders at temperatures of 1700 and 1900°C for 15 min respectively resulted in relative densities of 84.9 and 97.1 %. This indicates that SPS of niobium boride powders needs more temperatures than 1500°C to obtain full densification. Nevertheless, Co addition during pressureless sintering contributes to the density values of the samples more than SPS sintering at the same temperature of 1500°C. All the relative density values conform well to the microstructures presented in the OM and SEM images of the samples (Figure 4.42 and 4.45). It can be also interpreted that both the use of sintering temperature higher than 1500°C and the use of Co sintering aid during PS and SPS processes will yield the highest relative density values for the samples.

**Table 4.5 :** Density values of the sintered vanadium and niobium borides.

| <b>Sample Name</b> | <b>Theoretical Density (g/cm<sup>3</sup>)</b> | <b>Archimedes Density (g/cm<sup>3</sup>)</b> | <b>Relative Density (%)</b> |
|--------------------|-----------------------------------------------|----------------------------------------------|-----------------------------|
| N5-PS              | 7.20                                          | 5.84                                         | 81.11                       |
| N9-PS              | 7.30                                          | 5.53                                         | 75.75                       |
| N5-2CoPS           | 7.03                                          | 6.59                                         | 93.74                       |
| N5-5CoPS           | 7.13                                          | 6.96                                         | 97.61                       |
| V7-PS              | 5.11                                          | 4.20                                         | 82.19                       |
| N5-SPS             | 7.20                                          | 6.03                                         | 83.75                       |
| N9-SPS             | 7.30                                          | 6.53                                         | 89.45                       |
| V7-SPS             | 5.11                                          | 4.61                                         | 90.22                       |

#### 4.4.2 Mechanical properties of the sintered samples

Mechanical properties are reported in terms of microhardness, wear characteristics, elastic modulus, indentation behaviour and fracture toughness of the bulk products. Microhardness values ( $HV_{0.2}$ ) of the sintered vanadium and niobium borides are presented in Table 4.6. As previously mentioned, indentation tests could not be applied to the V7-PS sample due to its heterogeneous microstructure containing holes and pores (Figure 4.42(e)). Pressureless sintered niobium borides exhibit the lowest microhardness values of around 1.9 and 6.8 GPa (N5-PS, N9-PS) among the samples. Sintered product originated from the 9 h of milled powders exhibits higher microhardness (6.8 GPa) than that of milled for 5 h (1.9 GPa). However, when the OM image of N9-PS sample is taken into consideration (Figure 4.42(b)), its microhardness cannot be regarded as an accurate value because the indents on this sample were only obtained from the highly densified regions. As seen from Table 4.6, microhardness of N5-PS sample (1.92 GPa) incredibly increases with Co addition during pressureless sintering and reaches to 24.82 and 27.17 GPa for the N5-2CoPS and N5-5CoPS samples, respectively. This phenomenon can be attributed to finer microstructures and higher densities of the N5-2CoPS and N5-5CoPS samples which consist of  $Nb_3B_4$  as the major phase and  $NbCo_2$  as an intermetallic phase. It has been previously reported that intermetallic phases distributed in a major boride phase contribute positively on the hardness values of the sintered products (Khanra ve Godkhindi, 2005). Furthermore, spark plasma sintered niobium borides (N5-SPS, N9-SPS) demonstrate much higher microhardness values as 13.68 and 16.06 GPa compared to those of pressureless sintered samples. Among the spark plasma sintered samples, the V7-SPS sample has the highest microhardness value of 18.03 GPa, which also has the highest relative density value of 90.22 %. Among all

samples, the N5-5CoPS sample has the highest microhardness value of 27.17 GPa, along with the highest relative density value of 97.61 %. Thus, the microhardness values of the samples are in the same trend with their density values: They increase when sintering method was changed from PS to SPS and they exhibit the highest values when Co was added in the case of using PS.

Bulk NbB<sub>2</sub> prepared by sintering of Nb and B powders at 1600°C for 15 min under 4 GPa resulted in a microhardness value of 25.5 GPa (Matsudaira et al, 1989). NbB<sub>2</sub> crystals prepared by the floating zone method exhibited the Vickers hardness values of HV<sub>0.2</sub>=19.1-21.7 GPa (Otani et al, 1998). Sairam et al (2014) reported the Vickers hardness of high density (with a relative density of 97.7 %) NbB<sub>2</sub> compacts, which prepared by SPS method (at 1900°C for 15 min under 70 MPa) from Nb and B powders, as HV<sub>0.1</sub>=20.2 GPa. NbC/NbB<sub>2</sub> compacts obtained from the MA-SHS and SPS at 1800°C for 10 min exhibited a microhardness value of HV=19.8 GPa with a relative density of 94 % (Tsuchida and Kakuta, 2006). NbB<sub>2</sub> grains in the B<sub>4</sub>C-NbB<sub>2</sub> composites produced by SPS at 1800-2200°C exhibited the microhardness values of HV<sub>0.1</sub>=~27 GPa and HV<sub>1.0</sub>=~22 GPa (Demirskyi and Sakka, 2014). Thus, SPS processes in the literature were applied between the temperatures of 1800-2200°C and the maximum microhardness was obtained as 21.7 GPa.

It can be stated that bulk niobium borides can have many different hardness values, depending on the method of synthesis, consolidation technique, the process parameters, and the relative density achieved. Comparing the reported hardness values of niobium borides with those of the present study, it can be stated that the achieved microhardness values are considerably high for the utilized consolidation processes (pressureless sintering with Co or SPS at 1500°C).

**Table 4.6 :** Microhardness values of the sintered vanadium and niobium borides.

| <b>Sample Name</b> | <b>HV<sub>0.2</sub> (GPa)</b> |
|--------------------|-------------------------------|
| N5-PS              | 1.92 ± 0.31                   |
| N9-PS              | 6.83 ± 2.17                   |
| N5-2CoPS           | 24.82 ± 2.06                  |
| N5-5CoPS           | 27.17 ± 1.85                  |
| N5-SPS             | 13.68 ± 0.73                  |
| N9-SPS             | 16.06 ± 1.58                  |
| V7-SPS             | 18.03 ± 2.26                  |

Wear volume loss and relative wear resistance values of the selected vanadium and niobium boride samples are presented in Table 4.7. As seen from Table 4.7, N5-PS sample has the highest wear volume loss of  $125 \times 10^{-4} \text{ mm}^3$  and a relative wear resistance of 1 as the reference. Relative wear resistance of the samples were calculated by dividing the wear volume loss of the N5-PS sample to those of the other samples. When Co is used as an aid of pressureless sintering (N5-2CoPS, N5-5CoPS), the relative wear resistances significantly increase to 44.6 and 27.8, along with the increase in the microhardness from 1.92 GPa to 24.82 and 27.17 GPa, respectively. The utilization of SPS also increases the relative wear resistance of niobium and vanadium boride samples to 10.9 and 39.1, respectively.

On the basis of these results, it is clear that wear resistances of the sintered samples are in the same increasing trend with their microhardness values, excepting the N5-5CoPS sample. The relation between wear volume amount and microhardness has been investigated by several researchers (Kumar et al, 2008; Balcı et al, 2014). The highest wear resistance was obtained for the N5-2CoPS sample among the samples and this is most likely due to the  $\text{NbCo}_2$  particles which restrict the flow of the material during sliding under an applied load. However, higher amount of  $\text{NbCo}_2$  particles in the N5-5CoPS sample than the N5-2CoPS sample causes a decrease in the wear resistance probably due to the contribution of third body wear of the released particles on the sliding surface. The decrease in the wear resistance of N5-5CoPS sample also indicates that wear volume loss is strongly dependent to the amount of intermetallic phase and this dependency limits the amount of addition of Co sintering aid, unlikely to the density and microhardness values.

The wear behaviours of the sintered vanadium and niobium borides are very limited in the open literature. Although many studies have been carried out on the wear properties of the boride-dispersed metal matrix composites, there are only few studies on the wear properties of the sintered transition metal borides (Ağaoğulları, 2014; Chakraborty et al, 2014). The wear volume loss of the N5-PS sample ( $0.0125 \text{ mm}^3$ ) exhibits almost similar value to those of the pressureless sintered samples originated from the mechanochemically synthesized rare-earth hexaboride powders ( $0.0102\text{-}0.0193 \text{ mm}^3$ ) and much lower value than those of the bulk samples originated from the commercial rare-earth hexaboride powders ( $0.2565\text{-}0.2627 \text{ mm}^3$ ) (Ağaoğulları, 2014). The values in Table 4.7 are also comparable to the wear

volumes of the hot-pressed  $\text{ZrB}_2\text{-TiB}_2$  ceramics which changed with varying amount of  $\text{TiB}_2$  and were reported between  $0.312 \times 10^{-4}$  and  $10.8 \times 10^{-4} \text{ mm}^3$  (Chakraborty et al, 2014).

**Table 4.7 :** Wear volume loss and relative wear resistance values of the sintered vanadium and niobium borides.

| Sample Name | Wear Volume Loss ( $\times 10^{-4} \text{ mm}^3$ ) | Relative Wear Resistance |
|-------------|----------------------------------------------------|--------------------------|
| N5-PS       | 125                                                | 1                        |
| N5-2CoPS    | 2.8                                                | 44.6                     |
| N5-5CoPS    | 4.5                                                | 27.8                     |
| N5-SPS      | 11.5                                               | 10.9                     |
| V7-SPS      | 3.2                                                | 39.1                     |

Figure 4.46(a)-(e) show the SEM images of the wear tracks taken at the same magnifications (80X) from the sintered vanadium and niobium borides. As seen from Figure 4.46(a), N5-PS sample has a very wide wear track, indicating the higher relative wear volume loss value than that of other sintered samples (Figure 4.46(b)-(e)). The high amount of the porosities in the microstructure of N5-PS sample probably lead to severe material loss during sliding due to the sliding motion of alumina ball under the applied load of 4 N. N5-PS sample exhibits some micro-grooves along the sliding direction whereas those of the N5-2CoPS, N5-5CoPS, N5-SPS and V7-SPS samples reveal almost smooth wear tracks. As seen from Figure 4.46(b),  $\text{NbCo}_2$  particles are preferentially aligned along the sliding direction which considerably reduces the ploughing tendency of the counterface.

Furthermore, the smooth appearance of the worn surfaces of the spark plasma sintered samples (N5-SPS, V7-SPS) can also be explained by the resistance against material removal in the sliding surface due to their high density and high hardness values.

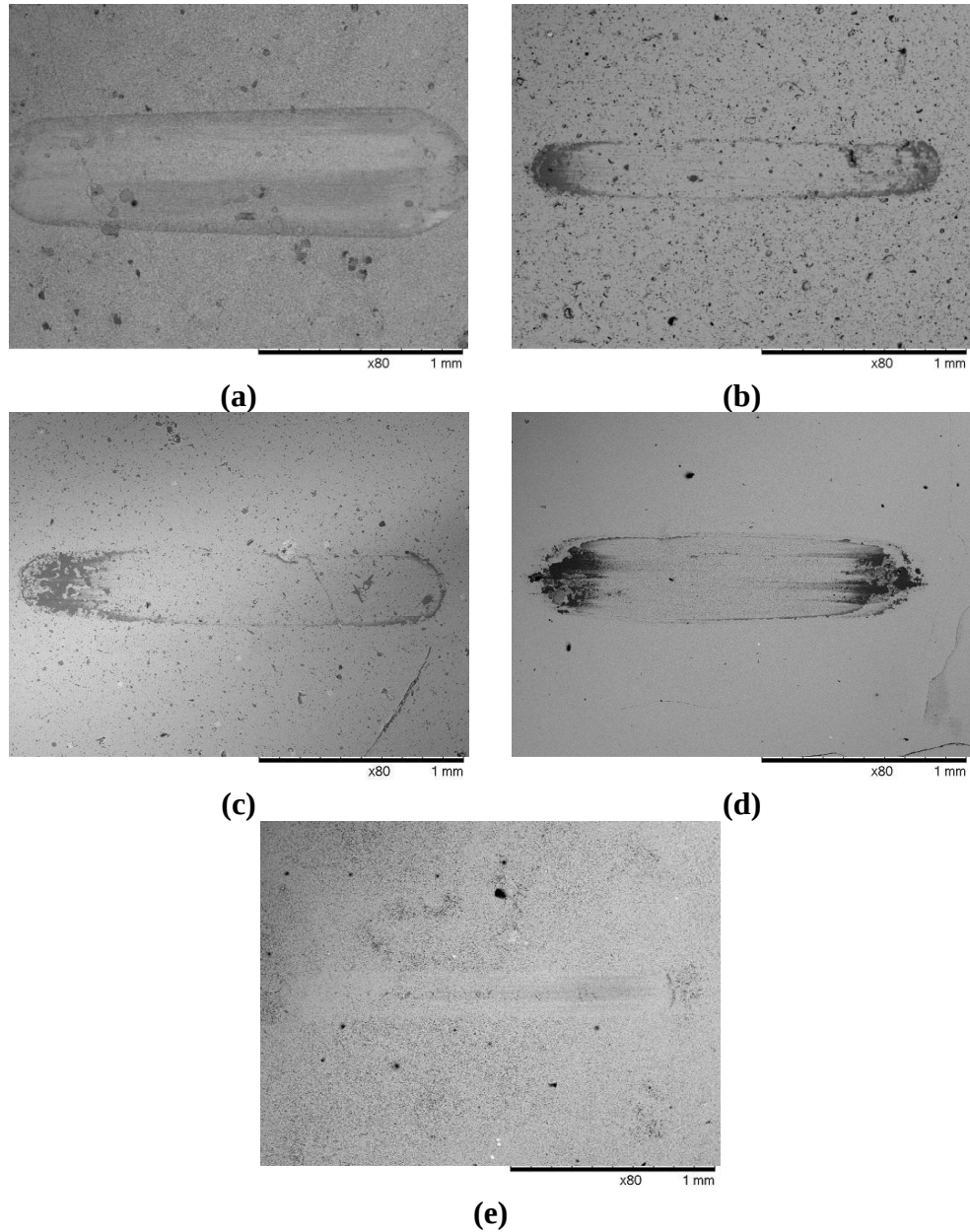


**Figure 4.46 :** SEM images of the wear tracks taken from the sintered vanadium and niobium borides: (a) N5-PS, (b) N5-2CoPS, (c) N5-5CoPS, (d) N5-SPS and (e) V7-SPS samples.

Figure 4.47 presents the mean friction coefficient values of the sintered vanadium and niobium borides. Friction coefficient of the sintered N5-PS sample sliding against alumina counterface is about 0.30 and the cobalt addition, which were independent of wt.% content, let to an increase in friction coefficient of about 0.48 for both of the N5-2CoPS and N5-5CoPS samples. The friction coefficient values and wear track appearances of the N5-2CoPS and N5-5CoPS samples suggest that these samples have similar friction characteristics. The highest friction coefficient value among the samples was obtained for the spark plasma sintered V7-SPS and

N5-SPS samples as 0.493 and 0.532, respectively. The results showed that pressureless sintering process without aid obviously reduced the friction coefficient during sliding action.

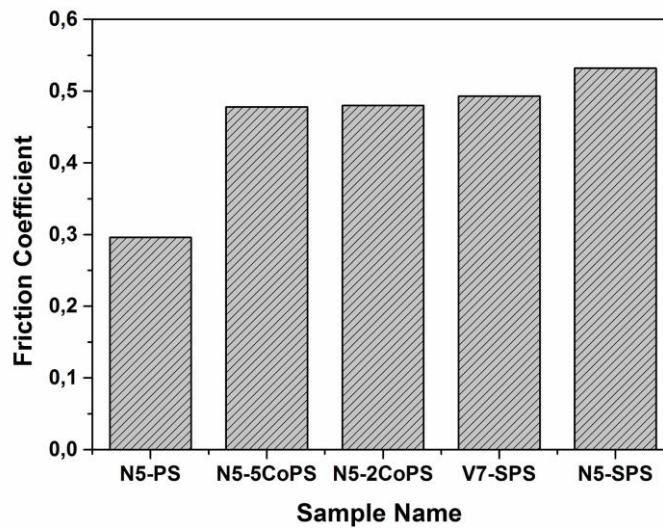


**Figure 4.47 :** Friction coefficients of the sintered vanadium and niobium borides.

In order to make a representative evaluation between the highest and lowest wear volume loss amounts among the samples (Table 4.7), the wear track profiles of the N5-PS and N5-2CoPS samples were compared to each other. Figure 4.48 shows the wear track profiles of the N5-PS and N5-2CoPS samples and contact surface OM images of the alumina balls slid on their surfaces. The comparative wear profiles of N5-PS and N5-2CoPS samples clearly reveals the influence of microstructural characteristics on the wear volume amount of the sintered samples. N5-PS sample shows a very high wear track depth which results in high material loss and low wear resistance, whereas a very low wear depth is observed in the N5-2CoPS sample. As seen from OM images in Figure 4.48(b), the worn surface of the alumina ball slid on the surface contained parallel scratches, which are the main characteristics of micro-abrasion. The contacting surface of the balls seems to be flattened along the sliding direction, indicating its wear and adherence to the surface of the sample. Thus, it is also suggested that the worn surface of the N5-PS sample has a higher amount of aluminium and oxygen contamination than that of N5-2CoPS sample due to the increase of the contact surface of the ball during sliding on the surface of N5-PS sample. The worn surfaces of the alumina balls are seen as compatible with the SEM images of the wear tracks in Figure 4.46(a) and (b).

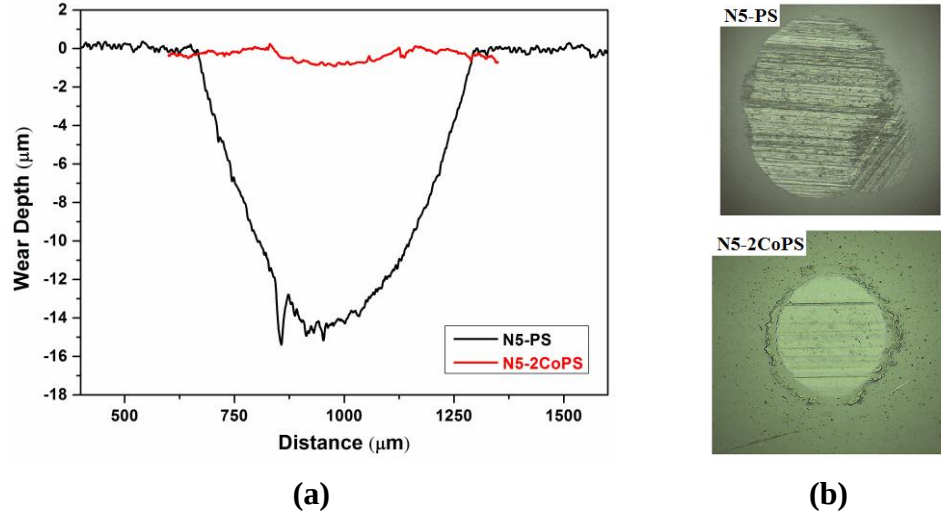


**Figure 4.48 :** Wear amounts of the N5-PS and N5-2CoPS samples: (a) wear profiles and (b) contact surface OM images of the alumina balls slid on the surfaces.

Figure 4.49 presents the load versus penetration depth curves of the sintered niobium borides obtained from the depth-sensing indentation measurements which were conducted under a maximum load of 250 mN with a constant loading and unloading rate of 500 mN/min. As seen in Figure 4.49, the curve of N5-PS sample shifts to lower indentation depths with the utilization of SPS and Co addition prior to pressureless sintering, indicating an increase in the indentation hardness. The area covered by the load-penetration depth curves reveals amount of the plastic deformation dissipated during indentation, which can be termed as residual plastic work (Mukhopadhyay et al, 2009; Genç et al, 2012).

It can be clearly observed in Figure 4.49 that the N5-PS sample has the highest plastic deformation among the samples and the residual plastic work significantly decreases to lower values for the N5-2CoPS, N5-5CoPS and N5-SPS samples. As also seen in Figure 4.49, the N5-2CoPS and N5-5CoPS samples show very similar features of load-penetration depth curves, which indicates that addition of high amount of Co during sintering has almost no effect on the residual plastic work and the penetration depth of the Vickers indenter.

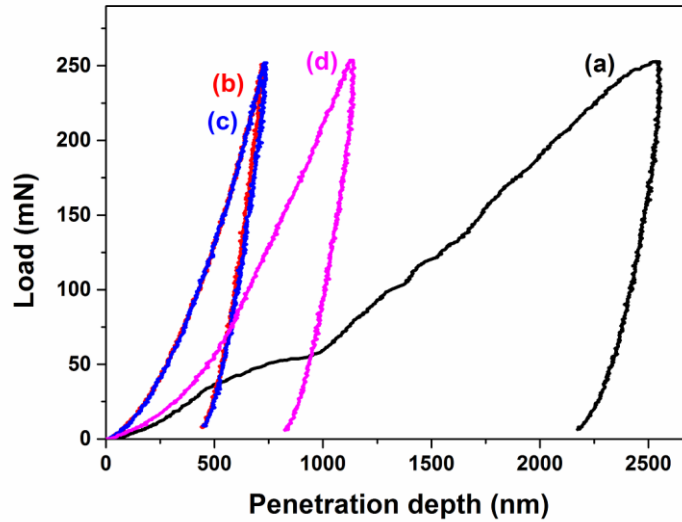


**Figure 4.49 :** The load versus penetration depth curves of the sintered niobium borides: (a) N5-PS, (b) N5-2CoPS, (c) N5-5CoPS and (d) N5-SPS.

Elastic modulus and fracture toughness values of the sintered niobium borides are presented in Table 4.8. Increasing indentation derived recovered elastic work as shown in Figure 4.49 with the utilization of SPS and Co addition prior to pressureless sintering is also reflected by the increase in the elastic modulus values as given in Table 4.8. There is a good correlation between the elastic modulus and the microhardness values of the samples, except the elastic modulus of the N5-5CoPS sample is slightly low considering its higher microhardness value than the N5-2CoPS sample. The relatively high amount of NbCo<sub>2</sub> particles dispersed in N5-5CoPS sample may cause a slight decrease from 552.2 GPa to 508.8 GPa in the elastic modulus of the N5-5CoPS sample. It has been also reported that the increase in weight percentages of MoSi<sub>2</sub> and TiSi<sub>2</sub> additives in some boride ceramics decreases the elastic modulus (Mukhopadhyay et al, 2009).

**Table 4.8 :** Elastic modulus and fracture toughness of the sintered niobium borides.

| Sample Name | Elastic Modulus<br>(GPa) | Fracture Toughness<br>(MPam <sup>1/2</sup> ) |
|-------------|--------------------------|----------------------------------------------|
| N5-PS       | 88.7                     | -                                            |
| N5-2CoPS    | 552.2                    | 4.48 ± 0.56                                  |
| N5-5CoPS    | 508.8                    | 5.41 ± 0.29                                  |
| N5-SPS      | 243                      | 3.20 ± 0.17                                  |

Vickers indents obtained with a load of 0.2 kg did not result in the formation of cracks; however, increasing the indentation load to 2 kg resulted in extensive crack growth and enabling the evaluation of K<sub>IC</sub>. Indentation cracks of the N5-2CoPS, N5-

5CoPS and N5-SPS samples at the load of 2 kg were presented in the OM images given in Figure 4.50. Fracture toughness tests (using 2 kg indentation load) could not be conducted on the N5-PS sample because the cracks were not occurred. As seen from Figure 4.50(a)-(c), N5-5CoPS sample has lower crack propagation than those of N5-2CoPS and N5-SPS samples. The presence of higher amount of NbCo<sub>2</sub> particles in the N5-5CoPS sample can restrict the propagation of the diagonal cracks. Thus, as expected, the highest fracture toughness value of  $5.41 \pm 0.29 \text{ MPam}^{1/2}$  among the samples was obtained for the N5-5CoPS sample (Table 4.8).

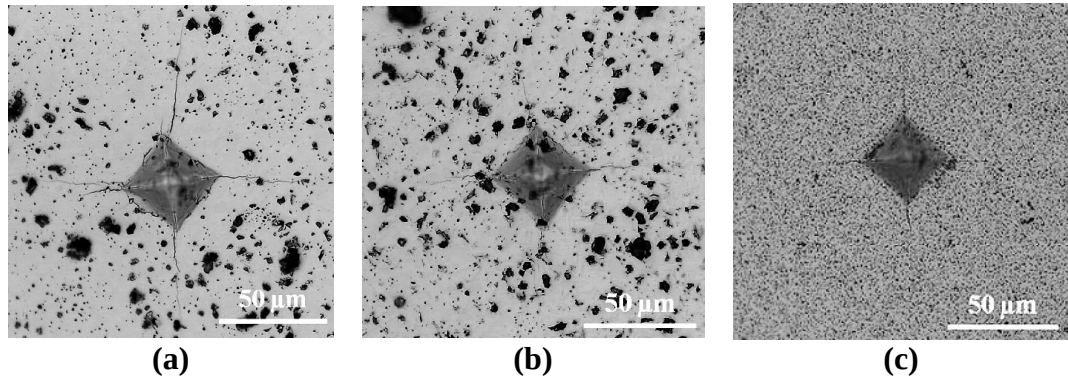


**Figure 4.50 :** OM images of the indentation cracks at a load of 2 kg: (a) N5-2CoPS, (b) N5-5CoPS and (c) N5-SPS.

NbB<sub>2</sub> compact produced by SPS of Nb and B at 1900°C for 15 min exhibited the Vickers hardness, fracture toughness and elastic modulus of 20.2 GPa,  $4 \text{ MPam}^{1/2}$  and 539 GPa, respectively (Sairam et al, 2014). NbB<sub>2</sub> grains in the B<sub>4</sub>C-NbB<sub>2</sub> composite fabricated by SPS exhibited a fracture toughness value of  $3.4 \pm 0.4 \text{ MPam}^{1/2}$  (Demirskyi and Sakka, 2014). NbB<sub>2</sub>-SiC composites obtained at 2000°C with a relative density of 98 % had the elastic modulus of 501 GPa (Malek et al, 2013). The fracture toughness values are also comparable to those of the VB<sub>2</sub> layer which were calculated through Palmqvist and median/radial approaches and had the ranges of 2.1-5.9 and 1.7-3.4  $\text{MPam}^{1/2}$ , respectively (Tarakci et al, 2010). Comparing the elastic modulus and fracture toughness values of niobium borides with those of the present study, it can be stated that the achieved values are considerably high for the utilized consolidation processes and parameters (pressureless sintering with Co or SPS at 1500°C). The highest density and mechanical properties of the sintered vanadium and niobium borides reported in this dissertation can be summarized as followed: Vanadium boride bulk product was obtained by SPS at 1500°C for 15 min with a relative density of 90 %, microhardness of 18 GPa and wear volume loss of

$3.2 \times 10^{-4} \text{ mm}^3$ . Niobium boride bulk product was obtained by SPS at  $1500^\circ\text{C}$  for 15 min with a relative density of 83 %, microhardness of 14 GPa, wear volume loss of  $11.5 \times 10^{-4} \text{ mm}^3$ , elastic modulus of 243 GPa and fracture toughness of  $3.20 \text{ MPam}^{1/2}$ . Niobium boride bulk products were obtained by PS (at  $1500^\circ\text{C}$  for 4 h using 2 or 5 wt. % Co aid) with relative densities of 93-98 %, microhardness of 24-28 GPa, wear volume loss of  $2.8\text{-}4.5 \times 10^{-4} \text{ mm}^3$ , elastic modulus of 508-552 GPa and fracture toughness of  $4.48\text{-}5.41 \text{ MPam}^{1/2}$ .

Consequently, addition of Co sintering aid prior to pressureless sintering process enabled to produce sintered niobium and vanadium borides with superior properties rather than PS and SPS techniques, considering the density, microhardness, relative wear resistance, elastic modulus and fracture toughness results. The addition of higher amount of Co also results in a minor decrease in the relative wear resistance and elastic modulus values of the samples. However, the need of application area can designate the accurate usage of the Co addition in the samples, for latter investigations.

## 5. CONCLUSIONS

In this dissertation, two different solid-state synthesis methods were utilized for obtaining vanadium and niobium boride powders and two different sintering techniques were utilized for obtaining bulk vanadium and niobium borides. This dissertation focused on the fabrication of boride and boride-based composite powders in high-purity through an economical way from their oxide raw materials, consolidation of borides to investigate the final properties and characterization investigations of both powder and bulk samples.

Results and discussions were presented mainly in four sections including the mechanochemical and milling-assisted carbothermal synthesis of the powders and the consolidation of them by different sintering techniques. Firstly, the fabrication of vanadium boride powders was investigated through the mechanochemical reactions of  $V_2O_5$ - $B_2O_3$ -Mg powder blends in terms of varying milling times and  $B_2O_3$  or Mg contents. Secondly, the fabrication of niobium boride powders was investigated through the mechanochemical reactions of  $Nb_2O_5$ - $B_2O_3$ -Mg powder blends in terms of varying milling times, considering thermal behaviours and applying an additional annealing process. Thirdly, the fabrication of niobium boride-niobium carbide composite powders was investigated by mechanical milling of  $Nb_2O_5$ - $B_2O_3$ -C powder blends and subsequent annealing process in terms of varying milling times, annealing temperature and C content. Finally, sintering of the obtained vanadium and niobium boride powders in high qualities was carried out by cold pressing/pressureless sintering (without or with Co addition) and spark plasma sintering (SPS) techniques. The results were discussed regarding the effect of different production conditions and sintering methods on the consolidation behaviour, microstructure and mechanical properties of the bulk samples.

Based on the results and characterization investigations reported in this dissertation, the following conclusions can be drawn:

For the mechanochemical synthesis of the vanadium boride powders:

- Vanadium boride powders having  $\text{VB}_2$ -VB- $\text{V}_3\text{B}_4$  phases were fabricated in high purity without any intermediate phase and any impurity via mechanochemistry by mechanical milling of the  $\text{V}_2\text{O}_5$ - $\text{B}_2\text{O}_3$ -Mg powders for 7 h with 50 wt. % stoichiometric excess of Mg and subsequent leaching process.
- Mechanical milling of stoichiometric  $\text{V}_2\text{O}_5$ - $\text{B}_2\text{O}_3$ -Mg powder blends after 30 min resulted in the formation of  $\text{VB}_2$ , VB and MgO phases with the presence of  $\text{VO}_x$  and unreacted Mg. There were not any remaining elemental V or B and additional compounds between V-Mg, B-Mg, V-Mg-O, V-B-O, B-Mg-O, etc. in the detection limit of XRD. Extending milling time up to 9 h had no effect on the mechanochemical reaction since there was no change in the XRD patterns of the milled powders. Thus, using stoichiometric amounts of the initial powders was not appropriate for the mechanochemical synthesis of high-purity vanadium boride powders.
- The utilization of stoichiometric excess amounts of  $\text{B}_2\text{O}_3$  (50 wt. % excess) provided completing the reduction process of  $\text{V}_2\text{O}_5$  and  $\text{B}_2\text{O}_3$  and caused the disappearance of  $\text{VO}_x$  and Mg phases. However, some of the excess  $\text{B}_2\text{O}_3$  reacted with MgO to form the  $\text{Mg}_3\text{B}_2\text{O}_6$  phase. This result is also consistent with the thermodynamic calculations where the formation of  $\text{Mg}_3\text{B}_2\text{O}_6$  phase was predicted. After leaching of the powders with 4 M HCl, the peaks of VB as major phase and  $\text{VB}_2$ ,  $\text{V}_3\text{B}_4$  and small amount of  $\text{Mg}_3\text{B}_2\text{O}_6$  phases were identified.
- The utilization of stoichiometric excess amounts of Mg (25, 50 and 75 wt. % excess) resulted in the formation of  $\text{VB}_2$ , VB and MgO phases which indicated that the formations of  $\text{VO}_x$  and magnesium borate phases and unreacted Mg were prevented when Mg was used in excess amounts. When Mg was used in 75 % excess amount, the lubricating effect of  $\text{B}_2\text{O}_3$  decreased and the Fe contamination from milling media increased.
- The optimum Mg content in the initial powder blends was determined as 50 wt. % stoichiometric excess amounts to synthesize vanadium boride powders. After leaching of the powders with 4 M HCl, MgO was completely removed and the peaks of  $\text{VB}_2$  as major phase and VB and  $\text{V}_3\text{B}_4$  phases were identified. TEM investigations also revealed the presence of the hexagonal  $\text{VB}_2$  phase which was

detected as the dominant phase in the XRD pattern and also orthorhombic VB phase which was detected as the secondary phase in the XRD pattern.

- The average density value of  $4.96 \text{ g/cm}^3$  was achieved for the  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powders milled for 7 h with 50 wt. % excess of Mg after leaching, which is very close to the theoretical density of  $\text{VB}_2$ . On the basis of XRD, AAS, DSC, SEM/EDX analyses and density measurements, it was proved that the resultant powders did not include any contamination or other unwanted reaction products. The particle size measurement of the resultant  $\text{VB}_2\text{-VB-V}_3\text{B}_4$  powders exhibited the average particle size of 171 nm. BF images monitored by TEM analyses consisted of particles with sizes 100 to 400 nm, which conform well to the SEM analyses and particle size measurements.

For the mechanochemical synthesis of the niobium boride powders:

- Niobium boride powders having  $\text{NbB}$ ,  $\text{NbB}_2$  and  $\text{Nb}_3\text{B}_4$  phases in various amounts and single phase  $\text{NbB}$  powders with high-purity were successfully synthesized by using solid-state synthesis methods from related metal oxide raw materials in the presence of a strong reducing agent.
- Niobium boride and  $\text{MgO}$  phases were achieved after 2 h of milling in a high energy ball mill using stoichiometric  $\text{Nb}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$  and  $\text{Mg}$  powder blends. There were no remaining elemental Nb or B and no additional compounds between Nb-Mg, B-Mg, Nb-Mg-O, B-Mg-O, etc. in the detection limit of XRD. DSC scans of the milled powders did not have any exothermic and endothermic peaks corresponding to the formations of  $\text{MgO}$ , Nb and B phases because they already included niobium boride and  $\text{MgO}$  phases after mechanochemical synthesis.
- Subsequent leaching with 4 M  $\text{HCl}$  enabled to remove the unwanted  $\text{MgO}$  phase and to obtain pure  $\text{NbB-NbB}_2\text{-Nb}_3\text{B}_4$  powders. Fe impurity released from the milling media could be completely removed by  $\text{HCl}$  leaching as well as  $\text{MgO}$ . The purity of the niobium boride powders were confirmed by AAS, DSC, SEM/EDX analyses and magnetic measurements.
- The average particle sizes as about 219, 194, 197 and 166 nm were obtained for the powders milled for 3, 5, 7 and 9 h after leaching, respectively. Milling of the  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  powder blends for 3 h resulted in a significant decrease in the particle sizes from micro to nano-scales, even after the leaching process.

Additional milling of 6 h reduces the particle sizes from 219 to 166 nm in the resultant powders.

- Extended milling times up to 9 h changed the compositions of the final products after leaching, i.e. the amounts of NbB, NbB<sub>2</sub> and Nb<sub>3</sub>B<sub>4</sub> phases. The amounts of NbB<sub>2</sub> and Nb<sub>3</sub>B<sub>4</sub> phases in the total volume gradually decreased by increasing milling time from 3 to 9 h. A steady-state condition in the overall reaction was reached after milling for 3 h based on the XRD and DSC analyses. NbB was the dominant phase after milling for 5, 7 and 9 h and subsequent leaching.
- Single phase NbB powders were achieved by annealing of the purified powders (after milling for 5 h and subsequent leaching) at 1500°C for 4 h under Ar atmosphere.
- The removal of MgO and the formation of niobium boride phases after milling and leaching treatment were also supported by SEM/EDX analyses. Orthorhombic NbB phase was also identified by TEM investigations. Resultant niobium boride powders had an average particle size of ~200 nm which was proved both by particle size measurements and BF image monitored by TEM analysis.

For the milling-assisted carbothermal production of the niobium boride-based powders:

- NbB<sub>2</sub>-based composite powders comprising various amounts of NbC were fabricated in high-purity via the carbothermal route at reduced temperatures due to the effect of mechanical milling of stoichiometric powder blends.
- Mechanical milling of Nb<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub> and C powder blends provided crystallite refinement and uniform distribution of powder particles and hence an increase in the reactivity of the starting materials. The reaction mechanism of the Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-C system and the onset reaction temperatures during annealing were highly affected by the milling process due to the highly activated C particles. Endothermic peaks in the DSC scans of the milled powders corresponded to the formation of NbC, in which two reaction steps concurrently took place without causing the emergence of the NbO<sub>2</sub> phase.
- The reaction between Nb<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub> and C occurred after annealing at 1300°C for 12 h by means of a holding time at this temperature. The NbB<sub>2</sub> phase could be

obtained by a milling-assisted carbothermal process at 1300°C, which is lower than the predicted formation temperature obtained from thermodynamical calculations.

- XRD analyses showed that the amount of the formed NbB<sub>2</sub> phase increased and that of the NbC phase decreased significantly by increasing the milling time and annealing temperature. Moreover, milling contributed to the elimination of residual C from the final powder without any post-treatment process, when stoichiometric amounts of the initial powders were used. Thus, annealing of the milled powders was more effective than annealing of the as-blended powders. The highest amount of NbB<sub>2</sub> was obtained from the powders milled for 5 h and annealed at 1400°C for 12 h.
- SEM investigations revealed that as-blended powders had irregular agglomerates presenting a heterogeneous microstructure, whereas 5 h of milled powders had a uniform microstructure provided by both the milling effect and the lubricating effect of the graphite particles. The SEM image of the powders after milling for 5 h and annealing at 1400°C clearly exhibited the formation of distinct particles having clear boundaries and irregular shapes in sizes between 500 nm and 3.5 µm. Elemental mapping of these powders confirmed the presence of NbB<sub>2</sub> and NbC phases in a single particle and the absence of any intermediate phase or impurity, in accordance with their XRD patterns.
- The neck formation arisen from a high temperature was proven via TEM analysis of the milled (for 5 h) and annealed (at 1400°C for 12 h) powders, which was taken as a proof of particle coalescence and hence grain growth observed in the SEM image. The BF image of a spheroidal-shaped particle is 600 nm in size, and the SADP taken from this particle verified the presence of the hexagonal NbB<sub>2</sub> phase, which also conformed well to the dominant phase in the XRD patterns.
- 100 % stoichiometric excess usage of C reducing agent decreased the formation temperature of niobium boride phase. However, the resultant powders could be obtained with the presence of residual C which requires a post-treatment process for the purification.

For the consolidation and bulk properties of the vanadium and niobium borides:

- Niobium boride powders originated from the mechanochemical reaction of  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  after milling for 5 and 9 h and HCl leaching were consolidated both by PS and SPS techniques without addition (N5-PS, N9-PS, N5-SPS, N9-SPS). Niobium boride powders originated from the mechanochemical reaction of  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  after milling for 5 h and HCl leaching were consolidated by PS using metallic Co sinter additive (2 and 5 wt. % of the total powder amounts) (N5-2CoPS, N5-5CoPS). Vanadium boride powders originated from the mechanochemical reaction of  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Mg}$  after milling for 7 h with 50 % excess of Mg and HCl leaching were consolidated both by PS and SPS techniques without addition (V7-PS, V7-SPS).
- The sinterability of the vanadium and niobium borides was improved by changing the sintering conditions and methods from PS to activated PS and SPS, based on the OM and SEM images and relative density values of the samples. The size and distribution of the pores in the pressureless sintered samples without aid (N5-PS, N9-PS, V7-PS) decreased substantially in the SPS samples (N5-SPS, N9-SPS, V7-SPS). Additional milling of 4 h during powder preparation did not make a significant change on the microstructures of the pressureless sintered (N5-PS, N9-PS) and spark plasma sintered (N5-SPS, N9-SPS) samples. PS of the powders with the presence of different amount of Co additive (N5-2CoPS, N5-5CoPS) provided the fine microstructures without any observable pore and segregation in the OM and SEM images (relative densities of 93-98 %).
- There was no contamination or other undesired phases in the microstructures of the bulk samples according to their XRD patterns. The significant change in the XRD patterns was detected in the PS samples with Co addition:  $\text{Nb}_3\text{B}_4$  as a dominant phase and a small amount of  $\text{NbCo}_2$  intermetallic phase were observed in the XRD patterns of the N5-2CoPS and N5-5CoPS samples, indicating that a reaction occurred between the dominant phase NbB and Co to form  $\text{Nb}_3\text{B}_4$  and  $\text{NbCo}_2$  during PS at  $1500^\circ\text{C}$  for 4 h. The reason of the formation of intermetallic phase instead of a secondary boride phase was attributed to the non-stoichiometric composition of the precursor powders. This unexpected formation of intermetallic phase was considered as an original result in the activated sintering of metal boride systems that led to a significant increase in the mechanical properties.

- Addition of Co sintering aid prior to PS process enabled to produce sintered niobium and vanadium borides with superior mechanical properties rather than PS and SPS techniques, considering the microhardness, relative wear resistance, elastic modulus and fracture toughness results. The addition of higher amount of Co also resulted in a minor decrease in the relative wear resistance and elastic modulus values of the samples.
- Pressureless sintered niobium borides exhibited the lowest microhardness values of around 1.9 and 6.8 GPa (N5-PS, N9-PS) along with their lowest relative densities respectively of 81 and 75 % among the samples. Microhardness of N5-PS sample (1.92 GPa) incredibly increased with Co addition during pressureless sintering and reached to 24.82 and 27.17 GPa for the N5-2CoPS and N5-5CoPS samples, respectively. Among the spark plasma sintered samples, the V7-SPS sample had the highest microhardness value of 18.03 GPa, which also had the highest relative density value of 90.22 %.
- Wear analyses revealed that N5-PS sample exhibited some micro-grooves along the sliding direction whereas those of the N5-2CoPS, N5-5CoPS, N5-SPS and V7-SPS samples revealed almost smooth wear tracks. When Co was used as an aid of pressureless sintering (N5-2CoPS, N5-5CoPS), the relative wear resistances significantly increased to 44.6 and 27.8, respectively. The utilization of SPS also increased the relative wear resistance of niobium and vanadium boride samples to 10.9 and 39.1, respectively. The highest friction coefficient values among the samples were obtained for the spark plasma sintered V7-SPS and N5-SPS samples as 0.493 and 0.532, respectively.
- Depth-sensing indentation measurements revealed that the N5-PS sample had the highest plastic deformation among the samples and the plastic work significantly decreased to lower values for the N5-2CoPS, N5-5CoPS and N5-SPS samples. Increasing indentation stiffness the load versus penetration depth curves with the utilization of SPS and Co addition prior to pressureless sintering was also reflected by the increase in the elastic modulus. The highest elastic modulus value of 552.2 GPa was obtained for the N5-2CoPS sample.
- Indentations forced with a load of 2 kg for the evaluation of fracture toughness value showed that N5-5CoPS sample had lower crack propagation than those of

N5-2CoPS and N5-SPS samples. The highest fracture toughness value of  $5.41 \pm 0.29 \text{ MPam}^{1/2}$  among the samples was obtained for the N5-5CoPS sample.

- As a conclusion, bulk vanadium boride product was obtained by SPS at  $1500^\circ\text{C}$  for 15 min with a relative density of 90 %, microhardness of 18 GPa and wear volume loss of  $3.2 \times 10^{-4} \text{ mm}^3$ . Bulk niobium boride product was obtained by SPS at  $1500^\circ\text{C}$  for 15 min with a relative density of 83 %, microhardness of 14 GPa, wear volume loss of  $11.5 \times 10^{-4} \text{ mm}^3$ , elastic modulus of 243 GPa and fracture toughness of  $3.20 \text{ MPam}^{1/2}$ . Bulk niobium boride products were obtained by PS (at  $1500^\circ\text{C}$  for 4 h using 2 or 5 wt. % Co aid) with relative densities of 93-98 %, microhardness of 24-28 GPa, wear volume loss of  $2.8\text{-}4.5 \times 10^{-4} \text{ mm}^3$ , elastic modulus of 508-552 GPa and fracture toughness of  $4.48\text{-}5.41 \text{ MPam}^{1/2}$ .

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## CURRICULUM VITAE



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- Reviewer Certificate, Elsevier Reviewer Recognition, 2014.
- Scientific Research Scholarship, German Academic Exchange Service, DAAD, 2012.
- Poster Award, 3<sup>th</sup> International Ceramic Glass Porcelain Enamel Glaze and Pigment Congress, Eskişehir, Turkey, 2014.
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- Young Scientist Award, 14<sup>th</sup> International Metallurgy and Materials Congress, İstanbul, Turkey, 2008.
- Deutsches Sprachdiplom, Staendige Konferenz der Kultusminister der Laender in der Bundesrepublik Deutschland, 2003.

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