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**PRODUCTION OF LEAD-FREE BRASS
ALLOYS, AND THE EFFECT OF SOME
ADDITIVES ON MACHINABILITY,
MECHANICAL AND CORROSION
PROPERTIES**

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ÖZET

KURŞUNSUZ PİRİNÇ ALAŞIMLARIN ÜRETİMİ ve BAZI KATKI MADDELERİNİN İŞLENEBİLİRLİK, MEKANİK VE KOROZYON ÖZELLİKLERİNE ETKİSİ

Anahtar Kelimeler: Kurşunsuz pirinç, İşlenebilirlik, Mikroyapı, Korozyon, Mekanik Özellikler.

Bu çalışmada kurşunun insan sağlığına olumsuz etkisinden dolayı, kurşun yerine döküm yöntemi ile MnS ve MoS₂ katkı maddeleri ilave edilerek üretilen kurşunsuz pirinç alaşımının işlenebilirlik, mekanik, mikroyapı ve korozyon özelliklerine etkileri araştırılmıştır. Ticari olarak temin edilebilen otomat pirinci (C36000) ve Ecobrass numuneleri referans olarak kullanılmıştır.

Ana alaşım elementleri 1100 ve 1150°C sıcaklık aralığında ergitilmiştir. Katkı maddeleri eriyik havuzuna eklenmiş ve sonraki adımda homojen bir mikro yapı elde etmek için grafit çubuk ile karıştırılmıştır. Son aşamada, hazırlanan alaşımın katılaşması için yüksek hız çeliği ile üretilmiş kalıba dökülmüştür.

Üretilen kurşunsuz pirinç alaşımlarının mikro yapıları alfa, beta ve intermetalik bileşiklerinden meydana geldiği X-Işını Kırınım analizi (XRD) ve Taramalı Elektron Mikroskopu-Enerji Dağılım Spektroskopisi (SEM-EDS) sonuçları ile kanıtlanmıştır. Mikroyapılarında bulunan morfojiler, katılaşma parametresi, katkı maddesi cinsi ve miktarına göre Widmanstatten, dendritik ve iri taneler olmak üzere üç farklı şekilde meydana gelmiştir. Beta fazı oluşumunun Si'nin varlığı ile desteklendiği ve artan Si miktarıyla mikro yapıda dubleks alfa-beta fazlarından tek beta fazına dönüştü tespit edilmiştir.

Sertlik testinin sonucunda mikroyapıda beta fazı artışının sertlik değerlerinin artmasına sebebiyet verdiğini ve ayrıca numunenin sertlik değerlerinin mevcut fazlardan ve dağılımlarından büyük ölçüde etkilendiği bulunmuştur.

Hazırlanan ve referans numunelerin işlenebilirliği, yüzey pürüzlülüğü ve talaş oluşumu açısından değerlendirilmiştir. Hem MoS₂ hem de MnS katkı maddeleri ile hazırlanan numuneden istenen süreksiz talaş türü elde edilmiştir. Ayrıca, mikroyapıdaki morfolojilerin işlenebilirlik üzerinde büyük etkisi olduğu gözlemlenmiştir. MoS₂ ilavesinin yağlayıcı etkisinden dolayı MoS₂ ile hazırlanan numunenin yüzey pürüzlülüğü değerinin, en düşük olduğu bulunmuştur. Hem referans numunenin hem de hazırlanan numunenin korozyon davranışının birbirinden farklı olduğu, MoS₂ ile üretilen alaşımların daha dirençli bir korozyon davranışı gösterdiği analiz sonuçlarında görülmüştür. MnS numunelerinin çekme mukavemeti ve yüzde uzaması EN 12164 standartlarına göre sınır değerlerine yakındır.

Aşınma testi sonuçları, MoS₂ ilavesi ile üretilen numunelerin düşük sürtünme katsayısına ve MoS₂'nin yağlayıcı etkisinden dolayı yüksek aşınma direncine sahip olduğunu göstermektedir.

Sonuç olarak, yeni geliştirilen MoS₂-2 numunesinin, şu anda endüstride ticari olarak kullanılan F.C.B ve Ecobrass ile aynı veya benzer özelliklere sahip olduğu belirlendi. Ek olarak MoS₂ ilavesi ile yeni geliştirilen pirinç alaşımının, iyi korozyon davranışına, daha iyi aşınma direncine ve düşük yüzey pürüzlülüğüne, olağanüstü düşük sürtünme katsayısına ve karşılaştırılabilir sertlik ve mekanik özelliklere ve uygun talaş şekline sahip, ümit verici kurşunsuz pirinç alaşımı olduğu görülmüştür.

ABSTRACT

PRODUCTION OF LEAD-FREE BRASS ALLOYS AND THE EFFECT OF SOME ADDITIVES ON MACHINABILITY, MECHANICAL and CORROSION PROPERTIES

Keywords: Lead-free brass, Machinability, Microstructure, Corrosion, Mechanical Properties

In this study, the effects of MnS and MoS₂ additives on the machinability, microstructural, mechanical and corrosion properties of lead-free brass alloys produced by casting method instead of lead alloying element due to the adverse effect of lead on human health were investigated. Commercially available Free-cutting brass (C36000) and Ecobrass alloys were used in production of reference samples.

The main alloying elements were melted at the temperature between 1100 and 1150°C. Additives were added into melt pool and stirred with graphite rod to obtain homogenous microstructure in the following step. Finally, molten alloy was poured and solidified into the mould, produced by high speed steel.

The microstructures of lead-free brass alloys produced have consisted of alpha, beta and intermetallic compound which was confirmed by the results of X-Ray Diffraction (XRD) analysis and Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS). The microstructure of lead free brass alloys revealed three different morphologies which are Widmanstätten, dendritic and coarse grains by virtue of solidification parameter, type and content of additives. From the view of phase transformation, the formation of beta phase was promoted by the existence of Si and Sn; in addition, duplex alpha-beta phase transformed to single beta phase in the microstructure with increasing Si content. Hardness value increased with increasing beta phase in microstructure; moreover, the hardness value of the samples was greatly affected by the distribution of phases.

The machinability of prepared and reference samples was evaluated in terms of surface roughness and chip formation. Chips obtained from the sample prepared with both MoS₂ and MnS additives is of the discontinuous type. In addition, morphologies in microstructure are found to have a great impact on machinability. The surface roughness value of sample prepared with MoS₂ additive was found to be the lowest due to its lubricity effect. Corrosion behavior of sample with MoS₂ addition were shown to be superior than reference samples. The ultimate tensile strength and elongation of MnS

samples are close to limit value according to EN 12164 standards. The wear test results show that the samples produced with the addition of MoS₂ have low friction coefficient and high wear resistance due to the lubricant effect of MoS₂.

Finally, it was determined that the newly developed MoS₂-2 sample had the same or similar properties as F.C.B and Ecobrass, which are currently commercially used in industry. In addition, the newly developed brass alloy with the addition of MoS₂ proved to be a promising lead-free brass alloy with good corrosion behavior, better wear resistance and low surface roughness, an exceptionally low coefficient of friction and comparable hardness and mechanical properties, and a favorable chip shape.



CLAIM for ORIGINALITY

The aim of thesis is to develop a new generation green brass which has been produced by casting technology to enhance machinability without Pb element, since it brings about health problem against the livings and pollution risk for the environment, especially in contact with soil and drinking water. In recent years, there have been various studies related to the lead-free brass alloys in the literature due to the adverse health effects of lead, new regulations and standards that restrict lead contamination to decrease the toxicity.

Ecobrass is one of the lead-free brass which is commercially used in industrial application. It is considered to be an alternative to Free Cutting Brass in which the presence of high silicon content leads to rapidly wear mechanism on tool tips, so increasing expenditure. In this case the market needs new generation lead-free brass alloys.

New generation brass alloy was developed, which can lead to innovative improvements in machinability, consists of hybrid, non-toxic, cost-effective production, easily available additives. In addition, this study would be anticipated to contribute to develop a domestic novel product, which may be an alternative lead-free brass alloy with a novel addition to provide better machinability and similar properties of lead-free brass alloys on the market. Moreover, it is emphasized that these findings can encourage new studies and future scientific research.

ABBREVIATIONS

FCC	: Face Centered Cubic
BCC	: Body Centered Cubic
HCP	: Hexagonal Close-Packed
Mg	: Magnesium
Sn	: Tin
Cu	: Copper
Zn	: Zinc
Be	: Beryllium
Si	: Silicon
Ni	: Nickel
Pb	: Lead
Bi	: Bismuth
Mn	: Manganese
Al	: Aluminum
Fe	: Iron
BUE	: Built up edge
α	: Alpha
β	: Beta
β'	: Beta prime
δ	: Delta
χ	: Chi
IMC	: Intermetallic Compound
SCC	: Stress Corrosion Cracking
SEM	: Scanning Electron Microscopy
XRD	: X-Ray Diffraction
EDS	: Electron Dispersive Spectroscopy
XRF	: X-Ray Fluorescence
FCB	: Free Cutting Brass

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1 INTRODUCTION

1.1 General Properties

Copper alloys are used in many industrial applications due to their excellent electrical, thermal conductivities and outstanding resistance to corrosion; exhibiting good formability; being nonmagnetic. Unalloyed copper is so soft and ductile that it is difficult to machine. However, mechanical and corrosion resistance properties of copper can be improved by alloying. Most copper alloys cannot be hardened or strengthened by applying heat-treatment procedure [1]. One of the commonly used copper alloys is brass of which the principal alloying constituent is zinc. Brass is a material with both strength and good fatigue resistance. Also, brass is cheaper than copper. Their properties are not only determined by proportion of zinc amount but also their strength, machinability and corrosion resistance can be enhanced by presence of additional element and their amounts. The Brass has various properties, such as

- Conductivity
- Strength
- Ductility
- Machinability
- Hardness
- Wear resistance
- Corrosion resistance

It is very suitable and economical for industrial applications by considering the formation of brass, because it can be easily casted, shaped, processed and fabricated.

Brass alloys are produced by melting pure copper and zinc together. Brass alloys containing more than 54% copper are widely used in industrial applications. Low-copper brass alloys have low mechanical properties and are brittle.

For many applications, brass is usually the first choice of material for home equipment, electrical and all precision engineering industries. Brass is specified because of the unique combination of properties that make it essential. This combination is matched by no other materials. The machinability of brass sets the standard by which other materials are judged. Brasses can easily be casted to shape or fabricated by extrusion, rolling, drawing,

hot stamping and cold forming. To suit every need, there are many standard compositions for brass with copper contents ranging from 58% to 95% [1].

1.2 Brass

Generally, most of brass alloys consist of three phases which are α , β and α - β duplex phase structures displaying excellent strength and elongation. These alloys are comparable to mild carbon steels. Figure 1.1 shows the binary Cu-Zn phase diagram. As shown in Figure 1.1, there is an example of peritectic phase transformation and also copper and zinc elements are soluble in the liquid form. In the solid form, solubility is limited by virtue of their differing crystalline structure, copper has face centered cubic lattice and zinc has the hexagonal close-packed lattice (HCP). The alpha (α) phase is stable for concentrations up to 39 wt. % zinc at 450°C. The α -phase is a face-centered cubic (FCC) solid solution has the same crystal structure as pure copper. At room temperature zinc solubility decreases up to approximately 35 wt. %. Their ductility is high, they can be easily cold worked. Increasing zinc content in brass makes both α -phase and β -phase are stable at room temperature. According to the peritectic reaction at a temperature of 902°C primary α phase solid solution and liquid form turn into β -phase solid solution which is a body-centered cubic (BCC). In the case of alloys with the concentration of Zn from 36% wt. to 56 the β -phase exists after the solidification. The atoms of Cu and Zn are randomly distributed in the lattice at elevated temperatures. Randomly aligned β -phase is transformed into the ordered hard and brittle β' -phase between 454 to 468 °C. The brass which containing 39 % wt. to 45 Zn results into heterogeneous structure which contains α -solid solution crystals and β' -phase crystals. The deformability of β' -phase at room temperature is more limited, comparing to that of the α -phase. It is, however; significantly more workable than the α -phase at elevated temperatures, and can be extruded into bars of complex section or hot forged in closed dies to three-dimensional complicated shapes [2].

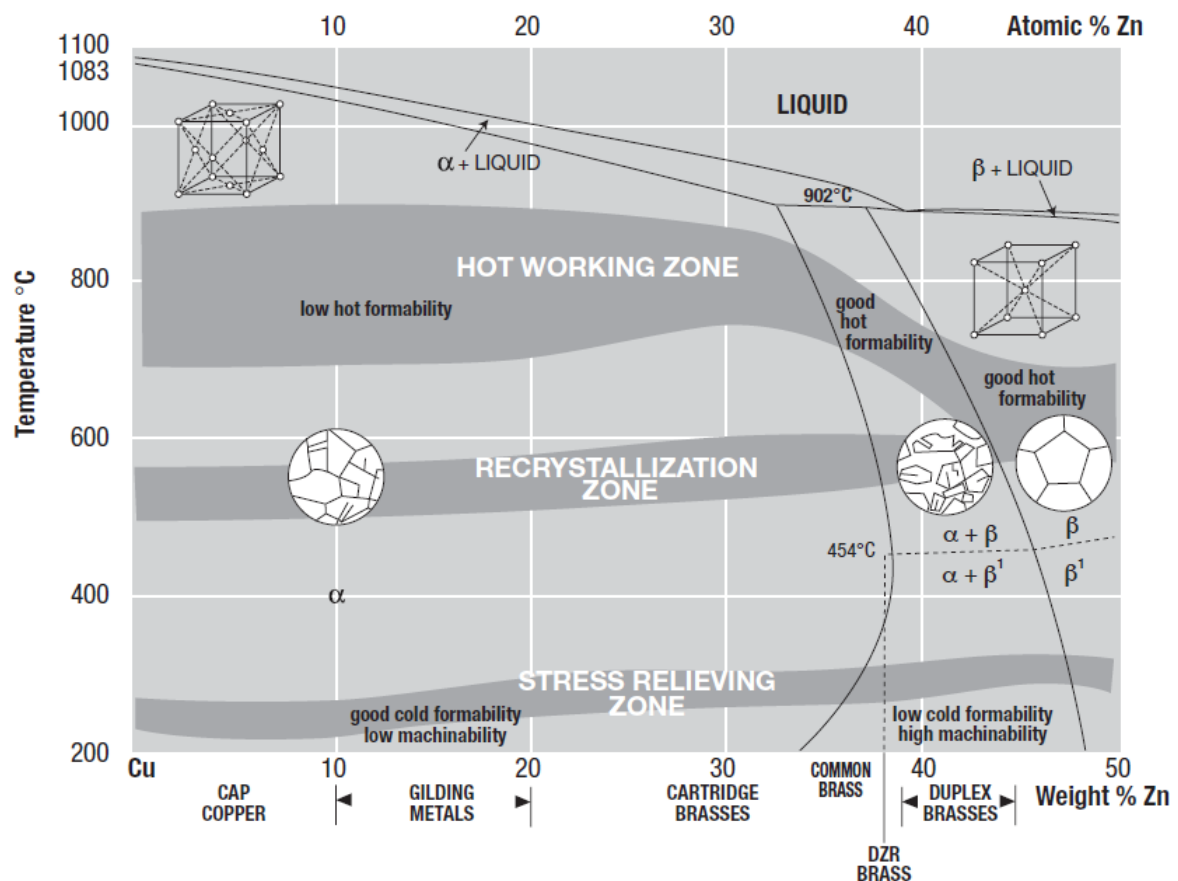


Figure 1.1 Binary copper-zinc phase diagram [3]

Besides α , β phases; ϵ , η , δ , γ phases appeared with increasing amount of zinc in the structure during solidification. Most of them are intermediate phases characterized by the relation of valence electrons and amount of atoms [2]. High zinc containing brass alloys give rise to brittleness, so they are not widely used in commercial applications.

Apart from the major alloying element zinc, less % wt. 5 other alloying elements than are added into brass to modify their properties so that the resulting material is ready for a given purpose.

1.3 Wrought Brass

They are suitable for shaping of metal sheets, tubes, wires, strips, bars. Forging and annealing processes can be applied to improve its ductility and increased their hardness subsequently by cold working.

More than 80% copper containing brass is called “tombac brasses”. Their physical and chemical properties are nearly same to pure copper, but their mechanical properties are

better than pure copper. Tombac brasses are used in various application areas such as decorative, artistic, imitation jewelry, architecture, armatures.

Deep drawing brass have high ductility due to the lower impurity element content which is used in musical equipment production and in food industry. One of the prominent deep drawing brass contains 30 wt. % zinc and is often known as '70/30' or 'cartridge' brass. CuZn30 - These alloys can be deep drawn for manufacture of cartridge cases.

With increasing amount of zinc, homogeneous alloy with α -phase turn into heterogenous alloy with α - β ' duplex phase. Compared to other brasses it exhibits higher strength properties, but lower ductility and cold forming ability due to the presence of high amount β ' phase at room temperature. It is suitable for forming at a temperature range of 700 – 800 °C. This kind of brass alloys is used as different forging products in ship construction, for tubes and welding electrodes. Brass with 60 wt.% of Cu content, is sensitive for dezincification corrosion and corrosion cracking. With increasing zinc value, there is a risk of cracking tendency and 40 wt. % Zn and over content is the highest risk region. This tendency disappears when the zinc content below 15 wt. %. Alloying elements do not change or improve the crack tendency. Alloying elements used for grain refinement reduce the cracking tendency because each grain boundary act as barrier [4].

1.4 Cast Brass

Castability of copper alloys are high and they are available to get many components via centrifugal casting, die casting, sand casting and continuous casting processes. Copper casting alloys are used for thermal and electrical apparatus, architecture parts, and gas and water armatures. Red and yellow brass are known the most common cast brass alloys which are used for plumbing system fixtures and hardware. Mechanical properties of cast brass are lower than mechanical properties of wrought brass because there are many defects like porosity and voids in the microstructure.

The casting process is used to produce complicated shapes. Range of end users is quite wide. Apart from these, long operation life with high strength components are required, which are used for their non-spark features and non-critical ornamental applications.

For all single-phase α alloys solidification begins with the formation of α dendrites on cooling below the liquidus temperature. Some coring occurs which allows the dendritic

structure to be visible in the microstructure after etching. The dendritic, as cast, structure is broken down by working and annealing to give twinned, equiaxed grains [5].

1.4.1 Tin Brass

One of the main additives is tin which is added to improve mechanical and corrosion properties of brass. (The range of tin addition is between 1 and 3 wt.% Ti). Tin is used to improve corrosion resistance in brass alloys because of forming a protective oxide layer. Some tin brass alloys are produced for music equipment due to their excellent acoustical properties. A large amount of tin content in brass alloys resulted in a brittle structure by virtue of existence of intermetallic phases. δ phase which reduces the ductility and induces decreasing in strength; on the other hand, their wear resistance is better by having heterogeneous structure due to $(\alpha + (\alpha + \delta))$ phase formation. During casting shrinkages of this brass is very low, approximately 1 vol. %, but this gives rise to feeding problems and increases in micro shrinkages in their microstructure.

1.4.2 Silicon Brass

Addition of silicon improves melting fluidity and it can be poured with a small degree of melting range. This type of brass is prone to pick up hydrogen thus overheating must be avoided. The maximum content of Si should be 4 wt.% in brass microstructure, so it can be shaped by forging or casting. They exhibit good corrosion behavior and mechanical properties at room temperature; on the other hand, silicon brass begins to be brittle at a temperature over 230°C.

1.4.3 Free Cutting Brass

Production engineers need to modify components which are produced by cast or wrought processes for final form. Machining process is one of the most used processes to final form. Most common brass has excellent high-speed machining operations and superior thread rolling and knurling characteristics. It is easily soldered and brazed and has very good resistance to corrosion. Evaluation of the machinability behavior is determined by their possessing machinability rate standard which is taken into account such as chip formation, surface roughness, cutting force and consumed power factors. It is rated as the highest 100 values in this standard. Machinability index between 100 and 70 is

appropriate for industrial application and are considered a good machinability. The addition of lead into brass alloys to improve machinability ranges from 1 to 3.5 wt %, and also depending on the alloying elements, this standard ratio ranges from 80 to 100 [6]. Brass alloys have high machinability rate standard compared to aluminum and steel alloys of the same strength [7]. Recently, the use of lead has been abandoned or limited to ppm level, since it has potential health hazardous against livings and environment. Furthermore, new legislation has obligated that restricting the usage of lead inside metallic material due to leaching of leaded effect into drinking water [8]. All these obligations have been pointed to the development of alternative alloys instead of lead in brass alloys. Silicon, bismuth, selenium and graphite is one of some new alternative additives.

1.4.4 Yellow Brass

Major alloying element in brass is zinc which has a content of between 23-41 wt. %. Other alloying elements are lead and tin which has a content of up to 3 wt.% and 1.5 wt.% respectively in the brass. The addition of aluminum prevents zinc vaporization as well as increases molten metal fluidity. When excess aluminum is added into brass, shrinkage takes place during solidification. But it can be tolerated using risers. Melting of brass is easy and there is no need to use fluxes during casting processes. Alloys turn into yellow color by the addition of varying amounts of zinc such as compositions ranging from the gold-like colors of the Cu/Zn ratio such as 95/5, 90/10, 85/15, and 80/20 alloys through more suitable variations in the 70/30.

Cold ductility of alloys in this composition region is very weak but hot workability is at the highest level due to the plasticity of the β -phase at elevated temperatures.

1.4.5 Red Brass

Red brass is known as copper alloys containing 2 – 15 wt % zinc. The other additional alloying elements are up to 5 wt. % of tin and up to 8 wt. % of lead. Castability is high and tapping temperature is the lowest one. Misruns and cold shuts are the most common defects that occur during the molten brass pouring stage into the molds in casting processes. Melting and tapping should be performed rapidly to reduce oxidation from the atmosphere; this ensures a good casting process.

However, there are some commonly used items made from such brass. Common products made of red brass include pumping equipment and sprinklers.

1.4.6 Naval Brass

This type of brass adapts well to hot forging and pressing and, it is suitable for drawing, forming, bending and heading. Weldability characteristic is better. It has excellent corrosion resistance to seawater at all temperature ranges while maintaining strength and rigidity.

1.5 Effect of Alloying Elements

1.5.1 Lead

Lead is used as an additive into brass in the range of 1 to 3 wt. % for improving machinability characteristics and ensuring pressure tightness. To produce bearing brass, a large amount of lead is added into copper. Lead is not soluble in copper, but it exists as a dispersed discontinuous phase and isolated particles in copper alloy, so the same effect occurs as in the case of leaded steels. Lead provides filling of pores by reducing solidification temperature. It does not influence corrosion resistance and mechanical properties. Lead is not added to wrought α -phase due to the absence of sufficient β -phase. It gives rise to cracking during hot working [3]. Thus, brass alloys containing 58 or 59 wt.% of Cu and lead are appropriate for several processes such as metal sheets, strips, bands and bars production and different shaped tubes without aggravating their mechanical and corrosion properties.

1.5.2 Aluminum

Aluminum is used in the range of 0.5 to 3.5 wt.% to have homogenous structure to prevent zinc vaporization and increase the tendency for the creation of new phases like β and γ in structure. Addition of aluminum decreases the ductility of brass alloys; however, it causes the most significant effect in increasing hardness and strength. One of the other positive effects of aluminum on brass alloy is improving corrosion resistance because aluminum shows self-healing and protective oxide film feature. Aluminum content in the brass alloys should not exceed 7 wt.%, because higher content leads to heterogeneous structure. For this reason, it is necessary to adjust optimum properties in a controlled manner.

1.5.3 Nickel

It is known that nickel and copper couple forms binary phase diagram and its system is a good example of isomorph system which liquid and solid solubility of its constituents are not limited; however, the range of nickel contain from 8 to 20 % wt. in the brass alloys due to the good cold formability. They completely dissolve in each component. This is called homogenous alloy which has better cold formability and appropriate for deep drawing. Nickel is used to improve hardness and strength without a major negative effect on ductility and to provide better mechanical properties of the alloy at high temperatures.

1.5.4 Silicon

Generally, silicon is used as a reducing agent and assisting fluidity in casting processes. It positively influences the strength and wear resistance of brass and also prevents zinc oxidation. Brass alloys contain up to 4wt. % silicon can be produced by forging but most of the silicon-containing brasses, a larger amount of copper approximately between 79 and 81 wt.%, can be produced by casting. Corrosion resistance and mechanical properties of them are good at low temperatures; conversely, they turn into brittle characteristics at a higher temperature. There is a combination tendency of Si with manganese to form a very hard intermetallic phase called manganese silicide which reduces the ductility of the brass

1.5.5 Manganese

Manganese addition improves strength and corrosion resistance of brass. 4 wt.% of manganese is enough to add for the production of brass by forging. Manganese can react with iron and aluminum resulting in an intermetallic phase which increases the strength of alloys. Furthermore, it is not harmful as an impurity, also used as a deoxidizing agent in casting processes.

1.5.6 Iron

Iron provides abrasion resistance by forming very hard intermetallic compounds in aluminum bronze brass. Addition of iron in the range of 0.5 to 2 wt.% into copper alloys increases to ability of forging but reduces machinability features. It is not desirable as an impurity in microstructure due to a negative effect on machinability. Both iron and copper induce the fine-grained structure and provide uniform dispersion of the lead in

microstructure. When the 6 wt.% iron content in brass is exceeded; toughness, elongation and corrosion resistance of brass are reduced.

1.5.7 Phosphorus

Phosphorus is added to copper up to 8 wt.% and its alloys for deoxidation as using a reducing agent and increase the hardness of the bronzes. It is added more than the amounts required for deoxidation. The addition of a small amount is enough to improve fluidity. High phosphorus content brings about porosity resulting from internal stress, thus the chemical composition is determined accurately so as not to cause residual stress.

1.6 The Selection of Furnace for Brass Alloying

There are three types of melting furnaces in terms of industrial application.

Electric arc furnaces have a wide range of products from large-scale melting to lab-type melting. It is suitable to produce cast iron production in small and medium sized foundries. Large volume foundries use it in the secondary steelmaking. Electric arc furnaces have adverse effects on the environment. While new installation costs are high, it also requires new systems to reduce losses and environmental effects. Flicker and harmonic distortion affected to common power system of furnace requires high technical measures to stably confirm power.

A cupola or cupola furnace is used to melt cast iron as well as produce Ni-resist iron. The cupola can be produced in the desired size. The shape of this device is usually cylindrical but can be produced in different sizes according to desire. It is sometimes very difficult to adjust the melting temperature in this type of furnace. Metal elements are converted to their oxide, so they become contaminated in the melting pool at high temperatures.

Induction furnaces can be relied on for requirements of industrial applications such as alloying and melting process. However, the efficiency of refining process is very low. Induction furnaces offer certain advantages over other furnace systems. The reasons of selecting the induction furnace are listed below:

Higher Yield: The absence of combustion sources reduces oxidation losses that can be significant in cost effective and economic production.

Faster Startup: Full power from the power supply is available, instantaneously, thus reducing the time to reach working temperature. Cold charge-to-tap times of one to two hours are common.

Flexibility: No molten metal is necessary to start medium frequency coreless induction melting equipment. This facilitates repeated cold starting and frequent alloy changes.

Natural Stirring: Medium frequency units can give a strong stirring action resulting in a homogeneous melt.

Cleaner Melting: No by-products of combustion mean a cleaner melting environment and no associated products of combustion pollution control systems.

Compact Installation: High melting rates can be obtained from small furnaces.

Reduced Refractory Consumption: The compact size in relation to melting rate means induction furnaces require much less refractory than fuel-fired melting units.

Better Working Environment: Induction furnaces are much quieter than gas furnaces, arc furnaces or cupolas. No combustion gas is present and waste heat is minimized.

Energy Conservation: Overall energy efficiency in induction melting ranges from 55 to 75 percent and is significantly better than combustion processes [9].

Our experimental studies are leaned on in alloying of brass by adding various non-toxic additives. Therefore, experimental studies in this study have been carried out with coreless-type furnace in regarding to compact installation, faster startup and flexibility.

1.6.1 Induction Furnace

The electric induction furnace is a type of melting furnace in which heat is applied via induction heating of metal to melt. Although induction furnaces are suitable for melting and alloying of a wide range of metals with high efficiency, they have very low refining and smelting process ability. The working principle of induction furnace is based on the induction heat which is a form of non-contact heating for conductive materials. The advantage of the induction furnace is a clean, energy-efficient and well-controllable melting process compared to most other means of metal melting units. Most modern foundries use this type of furnace and now also more iron foundries are replacing cupolas with induction furnaces to melt cast iron, as the former emit lots of dust and other

pollutant [10]. Induction furnace capacities range from less than one kilogram to one hundred tones capacity and are used to melt iron and steel, copper, aluminum and precious metals. Since no arc or combustion is used, the temperature of the material is no higher than required to melt it; this can prevent loss of valuable alloying elements [11]. Induction furnaces have increased in capacity to where modern high-power-density induction furnaces are competing successfully with cupola melting. There are fewer chemical reactions to manage in induction furnaces than in cupola furnaces. This makes it easier to achieve required melt composition. However, induction melting is more sensitive to quality of charge materials when compared to cupola or electric arc furnace limiting the types of scrap that can be melted [12].

1.6.2 The principle of Induction Furnace

The mechanism of induction furnace is mainly based on two physical phenomena which are known as electromagnetic induction and the joule effect respectively.

Electromagnetic induction is the production of an electromotive force across a conductor when it is exposed to a varying magnetic field. Electromagnetic induction which is the process of using magnetic fields to produce voltage and a current, is the basic principal of operation of transformers, motors and generators. Electromagnetic induction provides heat to be melted metal by transferring energy from source to object. Any electrically conductive material placed in a variable magnetic field is the site of induced electric currents, called eddy currents which will eventually lead to joule heating. This is illustrated in Fig. 1.2.

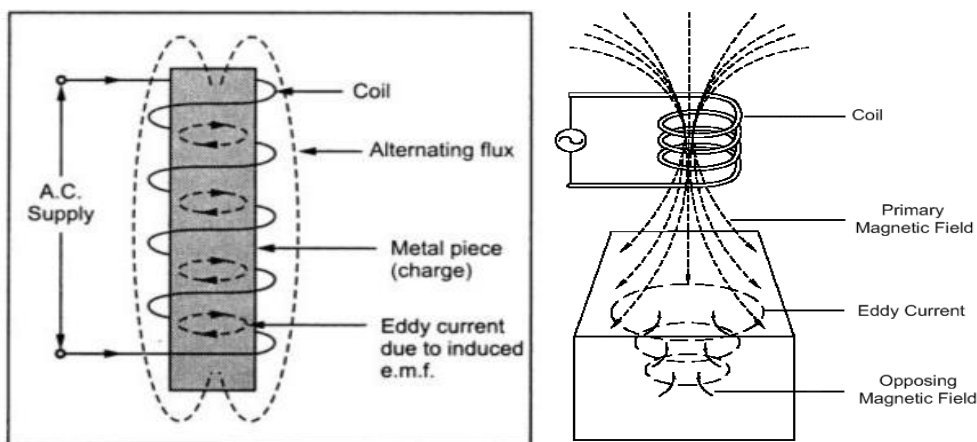


Figure 1.2 Generation of induction heating [15]

Joule heating occurs when an electric current pass through a conductor. Also known as resistance heating, this function simulates heating due to electrical resistance. The heat produced is proportional to the square of the current multiplied by the electrical resistance of the wire

$$Q \propto I^2 \cdot R \quad \text{Eq 1.1}$$

Where,

Q=Heat (joule), I= Current (A) R=Resistance (ohm)

Induction heating relies on the unique characteristics of radio frequency (RF) energy – the portion of the electromagnetic spectrum below infrared and microwave energy. Since heat is transferred to the product via electromagnetic waves, the part never comes into direct contact with any flame, the inductor itself does not get hot and there is no product contamination.

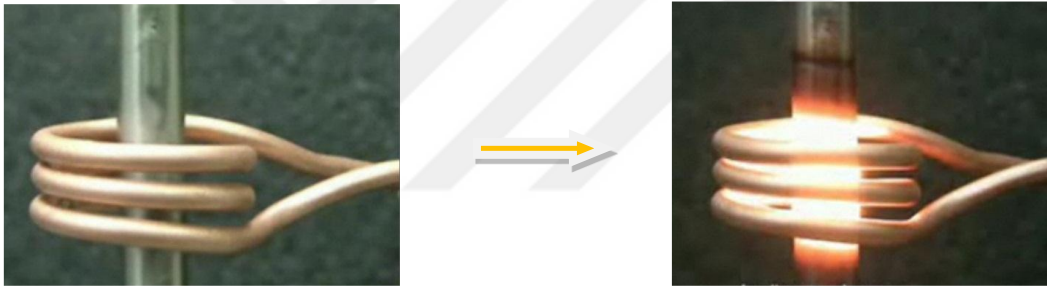


Figure 1.3 The effect of induction heating [13].

Induction heating is a rapid, clean and non-polluting heating method. The induction coil is cool to the touch; the heat that builds up in the coil is constantly cooled with circulating water. Figure 1.3 shows how induction heating operates before and after.

Operating frequencies range from utility frequency (50 or 60 Hz) to 400 kHz or higher, usually depending on the material being melted, the capacity (volume) of the furnace and the melting speed required. Generally, the smaller the volume of the melts, the higher the frequency of the furnace is used; this is due to the skin depth which is a measure of the distance an alternating current can penetrate beneath the surface of a conductor. For the same conductivity, the higher frequencies have a shallow skin depth that is less penetration into the melt. Lower frequencies can generate stirring or turbulence in the metal [14].

Induction furnaces generate their heat cleanly, without combustion. Alternating electric current from an induction power unit flows into a furnace and through a coil made of hollow copper tubing. This creates an electromagnetic field that passes through the refractory material and couples with conductive metal charge inside the furnace. This induces electric current to flow inside the metal charge itself, producing heat that rapidly causes the metal to melt [12].

Current flowing in one direction in the induction coil induces a current flow in the opposite direction in the metal charge. This current heats the metal and causes it to melt. Current flowing chart in the induction heating transformer is depicted in Figure 1.4

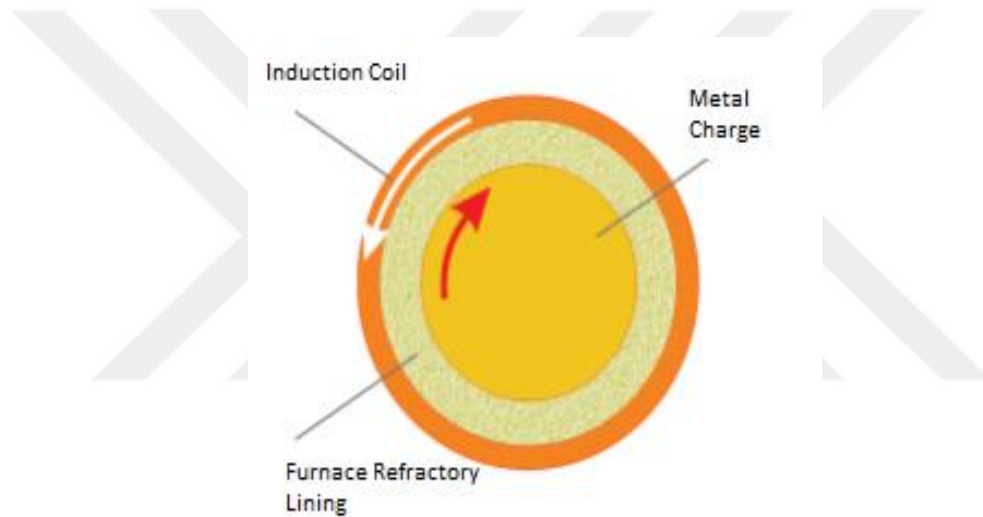


Figure 1.4 Current flowing chart in the induction heating transformer [12]

1.6.3 Types of Induction Furnaces

Basically, two different kinds of induction furnaces are used for melting, holding and casting of metals: the channel-type induction furnace and the coreless type induction furnace:

1.6.3.1 The channel-type induction furnace

The channel-type induction furnace is useful for small foundries with special requirements for large castings. It is widely used for duplexing operations and installations where production requirements demand a readily available molten metal [15].

This type of induction heating furnace uses the core type former. The metal core is linked to channel of molten metal as shown in Figure 1.5

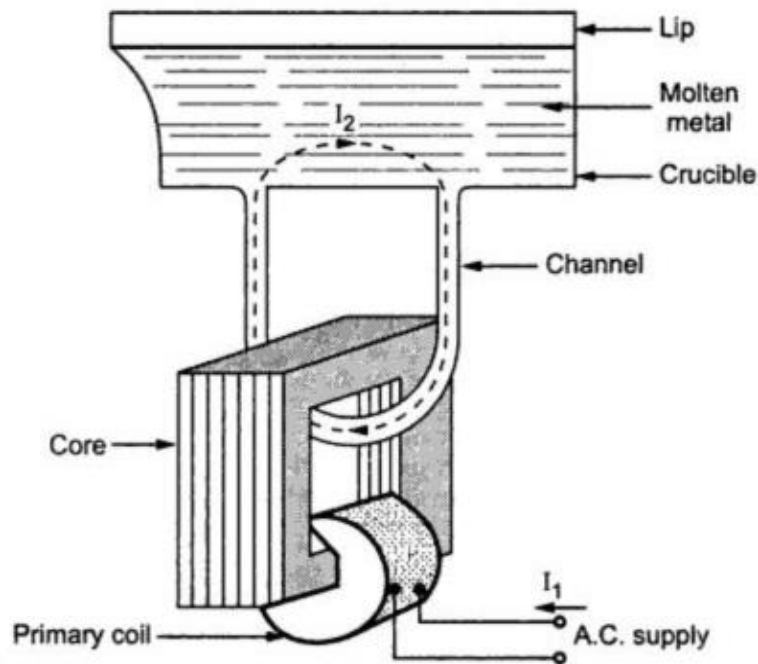


Figure 1.5 Channel-type induction furnace [15]

The ceramic pipe is used as a channel which is fitted to the bottom of the crucible. The channel acts as single turn short circuited on itself. The magnetizing current is low as flux is required to be driven through metal core having high permeability. The magnetic coupling between primary and secondary coil is poor which results into large leakage flux. To keep its minimum effect, the normal frequency supply is used.

1.6.3.2 The coreless-type induction furnace

Figure 1.6 shows coreless type induction furnace using transformer principle. It consists of a crucible of cylindrical shape with refractory lining. Primary winding is wound around crucible. The molten metal acts as a short-circuited secondary winding. The crucible can be of any convenient shape. The furnace is generally operated at high frequency. Due to this, skin effect exists which increase effective resistance of primary winding. Due to this fact, there are large current losses on copper and winding gets heated. Thus, primary winding is made hollow and water is circuited inside for cooling.

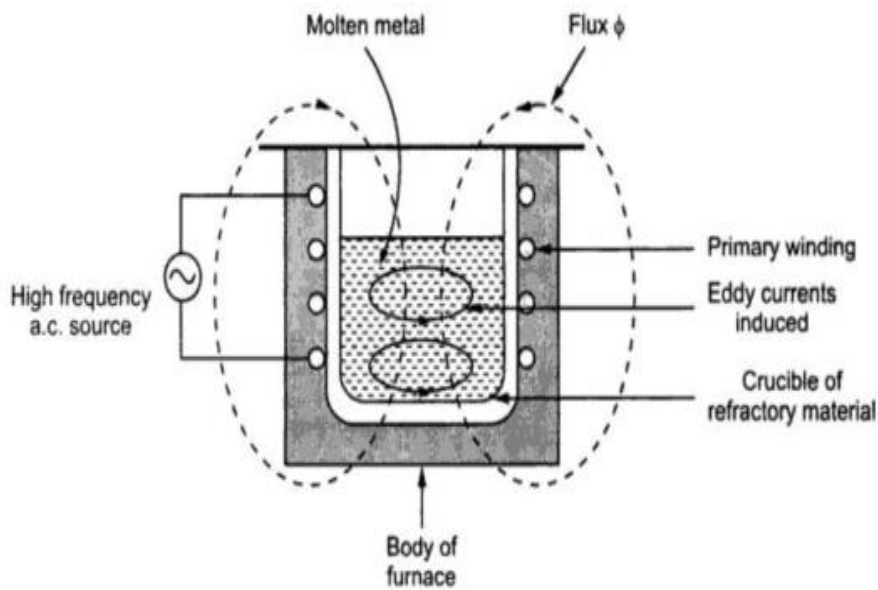


Figure 1.6 Coreless-type induction furnace [15]

The coreless induction furnace is used when a quick melt of one alloy is desirable, or it is necessary to vary alloys frequently. The coreless furnace may be completely emptied and restarted to melt easily [15].

The coreless induction furnace is commonly used to melt all grades of steels and irons as well as many non-ferrous alloys. The furnace is ideal for re-melting and alloying because of the high degree of control over temperature and chemistry while the induction current provides good circulation of the melt.

A channel furnace that holds and pours molten metal can operate efficiently using domestic frequency provided by the local authority. By contrast, most coreless furnaces for melting require a medium to high frequency power supply. Raising the frequency of the alternating current flowing through the induction coils increases the amount of power that can be applied to a given size furnace. This, in turn, means faster melting, 10 tones coreless furnace operating at 60 Hz can melt its capacity in two hours. At 275 Hz, the same furnace can melt the full 10 tones charge in 26 minutes, or four times faster. Another advantage of higher frequency operation is that furnaces can be started using less bulky scrap and can be emptied completely between heats [16].

1.7 Machining

Machining is one of the most important material removal processes by using cutting tool to produce the desired shape. Most semi-products such as castings and forged parts need machining processes to form final shape, besides many metal products are manufactured by this method which can also be used other materials such as ceramic, plastics and wood. Another reason for using machinability processes is, it is more cost effective and it contributes significantly to the Gross National Product.

When the cutting edge penetrated into the workpiece materials plastic deformation and extensive stresses take place on along the rake face of cutting edge in cutting processes. Considering primary manufacturing processes, machining is not an economical method on the other hand cost of cutting away is low and discarding unwanted chip formation and using these chips in recycling processes promotes economic improvements.

Machinability is a complicated process because there is no unambiguous clarity of the term. The machinability of materials differs from material to material and also can vary relying on material of cutting tools and its geometry. Cutting action in machining process includes shear deformation of work material to form a chip while removing chip. a new surface is revealed.

Employed machining techniques and machining conditions are most essential cutting parameters to effect machining criteria. It does not depend on a single categorized machining criterion thus machinability of copper and copper alloys are assessed in the way of four main machining criteria. These criteria can be listed including chip formation, cutting tool wear, surface quality and cutting forces. Despite fact that these four criteria do not interfere with each other mutually, the additional influence of factors such as conditions of workpiece, cutting conditions, special machining tool tips cannot impair machinability to certain criteria.

Tool wear means progressively removing material from surface of cutting tool and part or semi-product surfaces rubbing together which is resulted in changing of tool geometry. Wear is accompanied by large amount of friction all time, in sometimes plastic flow on subsurface of cutting tool. During machining process many factors such as adhesion, abrasion forces and high temperature provided by plastic deformation, mechanical stresses and surface fatigue enhance to tool wear mechanism.

Chip formation and chip type parameter play an important role in determining high productivity. Orthogonal cutting plane enables to examine chip formation in the machining processes because material flow can clearly be explained by this plane as well as machining operations and machining cutting processes can be described simply by this plane.

Cutting speed is relative velocity between the cutting tool and the surface of the workpiece. The following equation helps us determine the cutting speed. The cutting speed is an important parameter affecting surface quality in terms of workability. V_c refer to cutting speed; D_{cap} , workpiece of diameter; n , spindle speed. Schematic representation of the orthogonal cutting model is shown in Figure 1.7

$$V_c = \frac{D_{cap} \times \pi \times n}{1000} \quad \text{Eq. 1.2}$$

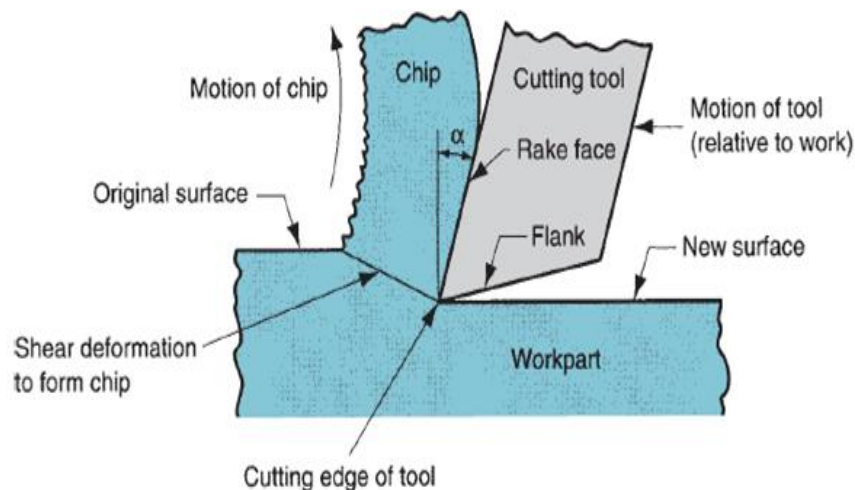


Figure 1.7 Machining Process-Cross Sectional View (Tool with positive rake angle) [17].

Even all of the sophisticated equipment and complicated techniques are very often used in industry, the main mechanics of forming a chip is the same [9]. The following factors are generally determined in assessing the machinability of materials [18].

- Cutting Tool Forces
- Chip Formation
- Cutting Tool Wear
- Surface Quality

1.7.1 Cutting Tool Forces

When enough force is provided or exposed to work material by tool, deformation takes place on work material and change the shape of work material. That means cutting force produced by tool's cutting edge and can be used to characterize machinability of materials. The design of the machine and cutting tools substantially affect cutting force.

Forces exposed by a tool during cutting affects mechanical structure of cutting machine, assisting to determine power consumption, estimating the tool life and augmenting the yield. Mostly cutting force is measured experimentally. It is important to predict how cutting parameters affect cutting force before starting machining operation for the following reasons:

- Design of cutting machine should endure to cutting force and thrust force effectively.
- Power consumption should be determined to select appropriate motor drive during machining process
- Predictable tool life
- Increasing productivity [18].

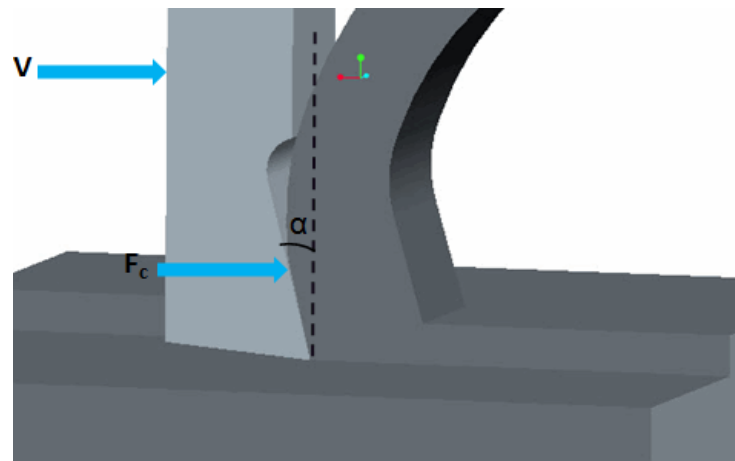


Figure 1.8 A tool under orthogonal cutting operation [19]

Important terminologies used in cutting force analysis are shown in Figure1.8. In this figure, a state in which the tool speed (V) and the cutting edge are perpendicular to each other is shown as an orthogonal cutting plane.

Acting on the cutting tool typically consists of three forces, they are tangential force, longitudinal force and radial force.

Tangential Force: This force provides a tangential force to the workpiece and at the same time represents resistance against the rotation of the workpiece. Tangential force accounts for high rate of the total power which is necessary for operation.

Longitudinal Force: This force acts in direction parallel to the axis of the work and also provides the resistance against the feed of the tool. The longitudinal force generally does not require the tool power as much as the tangential force but needs about half of it.

Radial Force: The smallest of three forces is radial force on which effective power needs is very little so radial direction of velocity is negligible [20].

1.7.2 Chip Formation

Chip formation is a process that occurs with plastic deformation regardless of tool being used for cutting. When a metal is exposed to unbearable load and exceeds its plastic limit, deformation takes place inside metal and it can be visualized as shearing.

Cutting operations, such as turning and milling includes in more cutting edges inclined at different angles to the direction of the cut. However, the basic mechanism of cutting can be clarified by analyzing cutting that is conducted with a single cutting edge. Orthogonal cutting model easily provides the details of chip formation process. Various chip segmentation form is illustrated in Figure 1.9.

The shape and size of the cutting formation is affected by mechanics of metal cutting and depended on the workpiece material and cutting conditions. It can be classified as four different chip formation as below [21].

- Discontinuous chip
- Continuous chip
- Lamellar chip
- Segmented chip

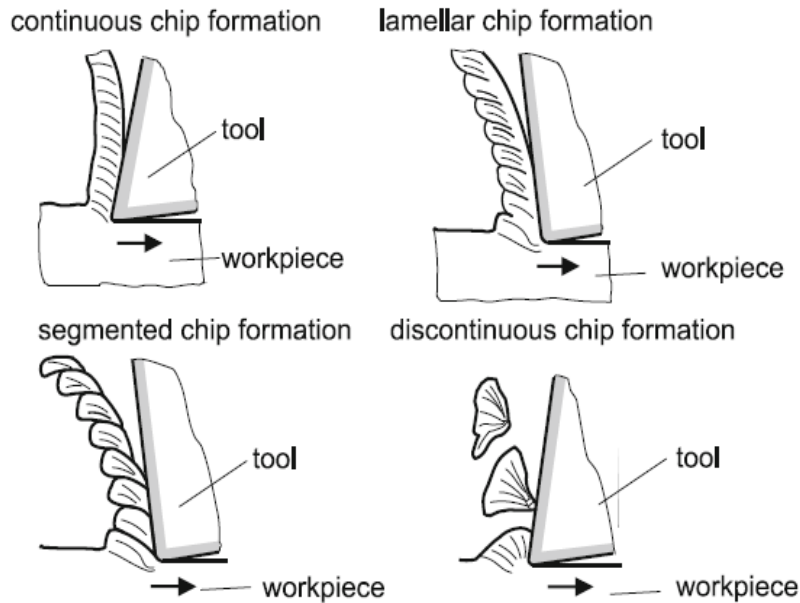


Figure 1.9 Mechanism of Chip Formation [22]

Discontinuous Chip: Generally brittle materials such as cast iron and hard bronze appear as this type formation of chip. Because brittle materials have lower ductility and high inhomogeneity, predefined slide paths are formed. When material is deformed, fracture easily takes place. That leads to chips produced in discontinuous form. When ductile metals are cut under weak cutting conditions, this type of chip formation is also obtained for work material's cutting surface.

When the cutting tool contacts the metal, some compression originates, and the chip starts flowing through the chip-tool interface. As more stress is applied to brittle material by the cutting action, the metal is compressed until it reaches limited point and the chip separates from the unmachined part. During cutting operation, this form enters to a cycle and repeated unlimitedly. The rupture of each segment arises from their shear angle or plane because of these consecutive ruptures, surface of workpiece has poor quality.

Continuous Chip: The chip slides off along the rake face at a constant speed in a stationary flow during cutting operation. Continuous chip generally is produced when ductile materials operated at high cutting speeds. According to efficient cutting action this type chip formation is ideal, and the surface quality is very good.

The factors that increase the formation of continuous chip are as follows:

- Uniform-grained structure
- High ductility of workpiece
- High cutting speed with low friction on the rake face
- Positive rake angles with low undeformed chip thickness

When machining of a highly ductile metal is performed at low cutting speed, it is extremely possible to lead formation of so-called built-up edge on head of cutting tool and rake face. First step, the metal ahead of the cutting tool begins to compress and chip flow along the chip-tool interface. Second, the high frictional resistance against the flow of the chip along the chip-tool interface can be resulted in high temperature and pressure. Final step, small particles of metal begin adhering to the edge of the cutting tool while the chip shears away and they become welded to the cutting tool face. The phenomenon results in a poor finish and damage to the workpiece due to changing geometry of cutting tool [21].

Lamellar Chip: This type chip formation is a periodic chip formation process like a continuous chip formation but deformed region on workpiece material is exposed to lamellar sliding without exceeding the shear strength of the material. Cleavage region and shear band result from impact of deformation. Lamellar chips take place with highly ductile workpiece metals with an increased strength especially at high cutting speeds.

Segmented Chip: This is a similar to discontinuous formation of a chip, but weakly connected elements and variations of chip form depend on degree of deformation along the flow path. This case usually takes place when using negative rake angle of cutting tools, discarding widely chip thickness and applying lower cutting speed [23].

Chip formation is based on two basic mechanisms in ductile and brittle materials.

- Yielding take places - usually for ductile materials.
- Brittle fractures appear in brittle materials

1.7.2.1 Mechanism of chip formation in machining ductile materials

During continuous processing, the uncut layer of working material immediately before the cutting material (edge) is subjected to almost all-sided compression. Because of this type of compression force, the shear stress grows in a varied direction and then follows with a substantially increased magnitude in that compression region. Whenever the value of the shear stress reaches or exceeds the cutting force of the work material in the deformation zone it results in the promotion of yielding and sliding in that region. However, the forces that cause shear stress in the chip region are rapidly reduced, and chips move towards the rake surface and then goes beyond the point of chip-tool connection and gets broken. This phenomenon is repeated quickly, resulting in the formation and removal of chips in the film's thin layer. This phenomenon is described simply by the Piispanen [24]. Serration taken place at tool's upper surface as delineated in Figure 1.10

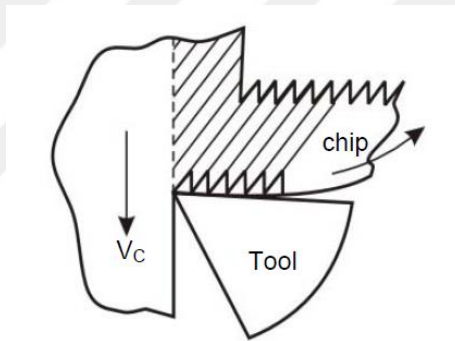


Figure 1.10 Lamella chip formation by shear force [25]

1.7.2.2 Mechanism of chip formation in machining brittle materials

Mechanism of chip formation for brittle materials is entirely different from ductile materials. During machining process, a small crack takes place inside the materials and is expanded by the tooltip by means of moving of the cutting edge. Stress concentration increases at the sharp side of the crack tip. Yielding taking place in the crack-tip for ductile materials results in reducing the effect of stress concentration. On the other hand, crack propagation is quickly initiated by augmentation of stress concentration at the brittle materials. The crack spreading in the material bring about the separation from the main material. Discontinuous chips in irregular size and shape are originated by machining of brittle material as depicted in Figure 1.11 and 1.12.

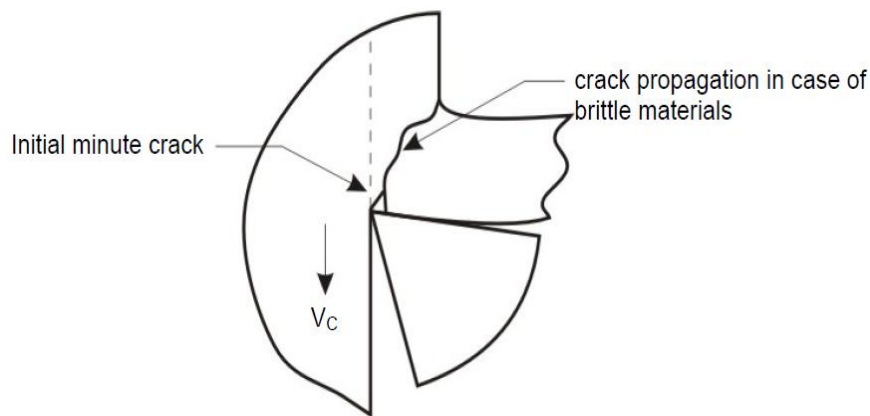


Figure 1.11 Propagation progress of chip separation for brittle materials [25]

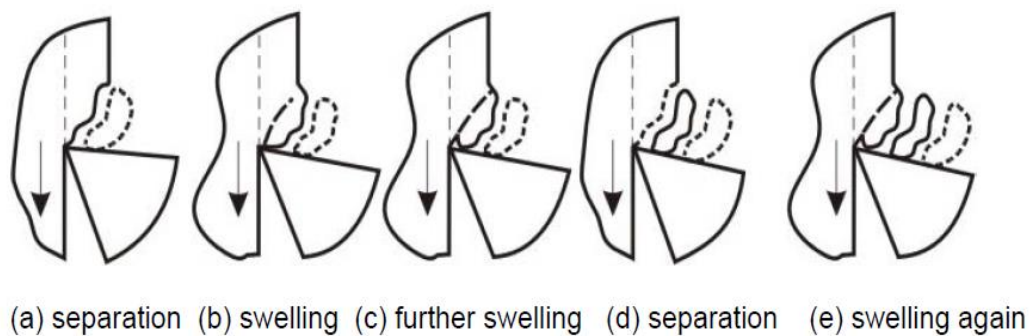


Figure 1.12 Schematic view of chip formation in machining brittle materials [25].

Figure 1.13 shows the ISO standard, supporting the importance of the cutting chip form for making coded classification possible.

The type, or often called the form of the cutting chip is an important feature of cutting processes. It influences:

- The stability of the process – e.g. long chips can disturb the machine, the environment and they have negative effect on the cutting process itself,
- The environmental effect of the production – e.g. small, broken chips are far easier to handle, store, transport and recycle.

1	2	3	4	5	6	7	8
RIBBON CHIPS	TUBULAR CHIPS	CORK SCREW CHIPS	HELICAL CHIPS	SPIRAL CHIPS	ARC CHIPS	ELEMENTAL CHIPS	NEEDLE CHIPS
							
Short	Short	Short	Short	Flat	Loose		
							
Long	Long	Long	Long	Conical	Connected		
							
Snarled	Snarled	Snarled	Snarled	Short			

Figure 1.13 Classification of commonly observed chip formation types according to ISO 6385-G1.

1.7.3 Cutting Tool Wear

One of the most important factors in the metal cutting process is the cutting tool life. To provide economical tool life, the appropriate tooling material, tool angle, cutter speeds, and feed rate are determined in operations. Conditions that give short tool life are not economical due to the high cost of tool change tool-grinding and indexing. Reducing cutting speeds and feed amounts will cause economic losses to occur despite increased tool life, resulting in lower production. Therefore, it is useful to take measures that prolong the tool life without a drop-in production. Understanding of the behavior of tool is very important to learn tool wear mechanism and forms of tool failure. The wear mechanisms vary depending on cutting conditions and cutting speeds. Wear marks appear

on the tool tip during operation. The wear of the tool varies depending on where the tool is exposed. Traces of wear generally appears on the side surfaces where the tool contacts the workpiece and where the chip is removed from the tool tip. The greater the amount of wear, the greater the mechanical and thermal stress experienced by the tool. The cutting tool material made by steel and by high-speed steel (HSS steel) retain its hardness at about 300°C and at about 600°C respectively. On the other hand, the cutting tool material made by cemented carbide maintain its hardness at about 1000°C.

In practical applications, type of wear on the tool's flank and face is determined main criteria to assess tool life. The type of wear introduced on the tool's flank is called flank wear land. The end of its useful service life is completed if width of flank wear has reached a specified limit. The width of the permissible flank wear land depends on the specific workpiece requirements [26].

When flank wear land grows, large face-side displacement of the cutting-edge increase and results in dimensional inaccuracies; moreover, an increase in the friction area between the tool and the workpiece results in higher cutting temperature and poor surface quality on workpiece.

Cutting speeds and cutting fluids affect the wear of the tool tip in different directions.

Except for the sudden break of the tool tip, there are physical indications of the progress of wear and these indications can be observed prior to rupture of edge by users. These indicators are as follows:

- Exceeding flank's wear land above limited value;
- Increase in crater depth and width in the rake face;
- Augmentation of power consumption and cutting force required for cutting operation;
- Exceeding the surface quality after machined part within a specified tolerance limit;
- Change in chip formation wear land and exceeding heat limited value;

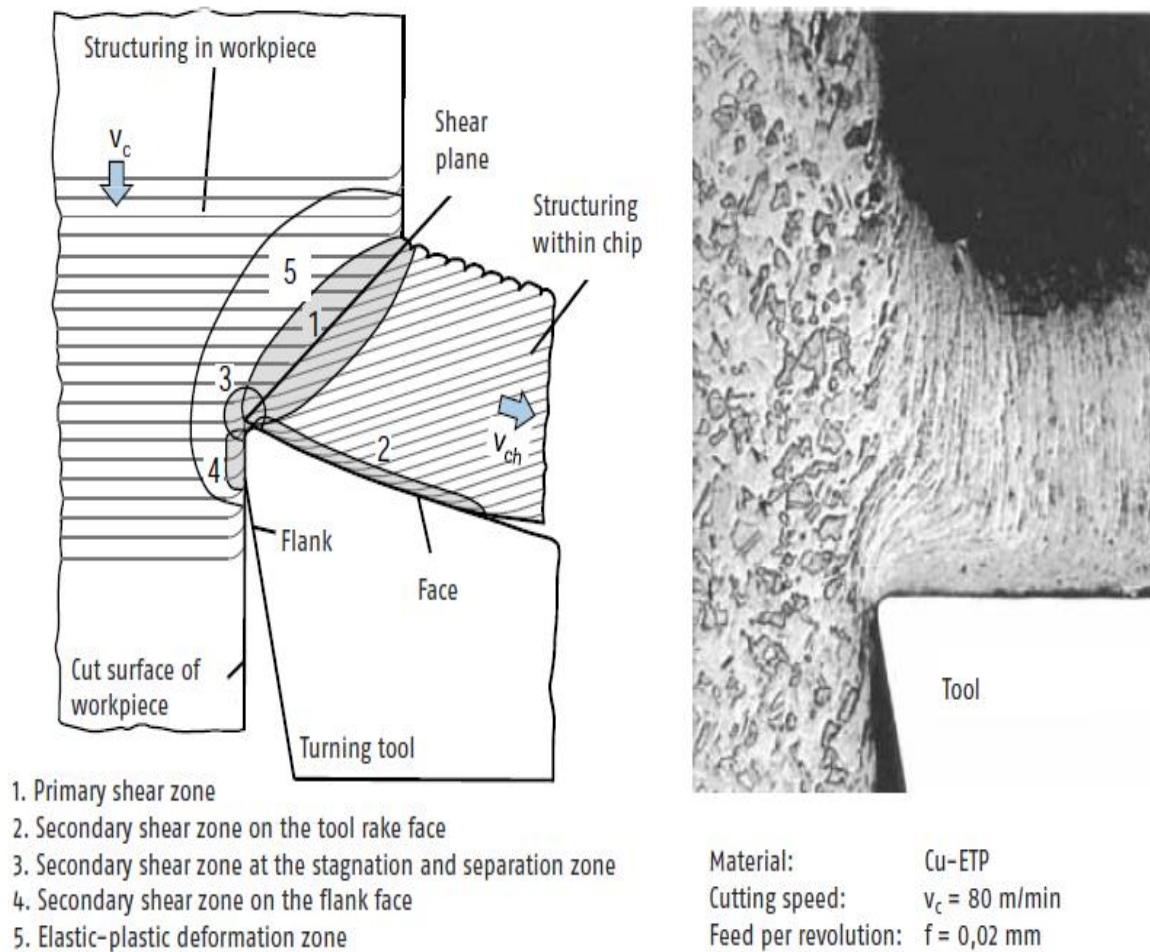


Figure 1.14 Material deformation zones during chip formation [27]

The region which contacts between tool and chip exhibits deformation zones during machining. One of them is plastic deformation which takes place on the tool rake face and chip surface. This is also called as Primary Deformation Zone (PDZ), Secondary Deformation Zone (SDZ) can also be identified in the metal cutting process. This occurs because of shear due to the contact friction conditions between the chip and the tool rake face. The deformation zones were presented in Figure 1.14 schematically.

Tool wear is the cause of tool failure, tool failure leads to failure of cutting tool. Wear of cutting tools depends on various parameters such as tool material, geometry, cutting parameters and workpiece materials. Figure 1.15 shows many types of failure and wear cutting conditions.

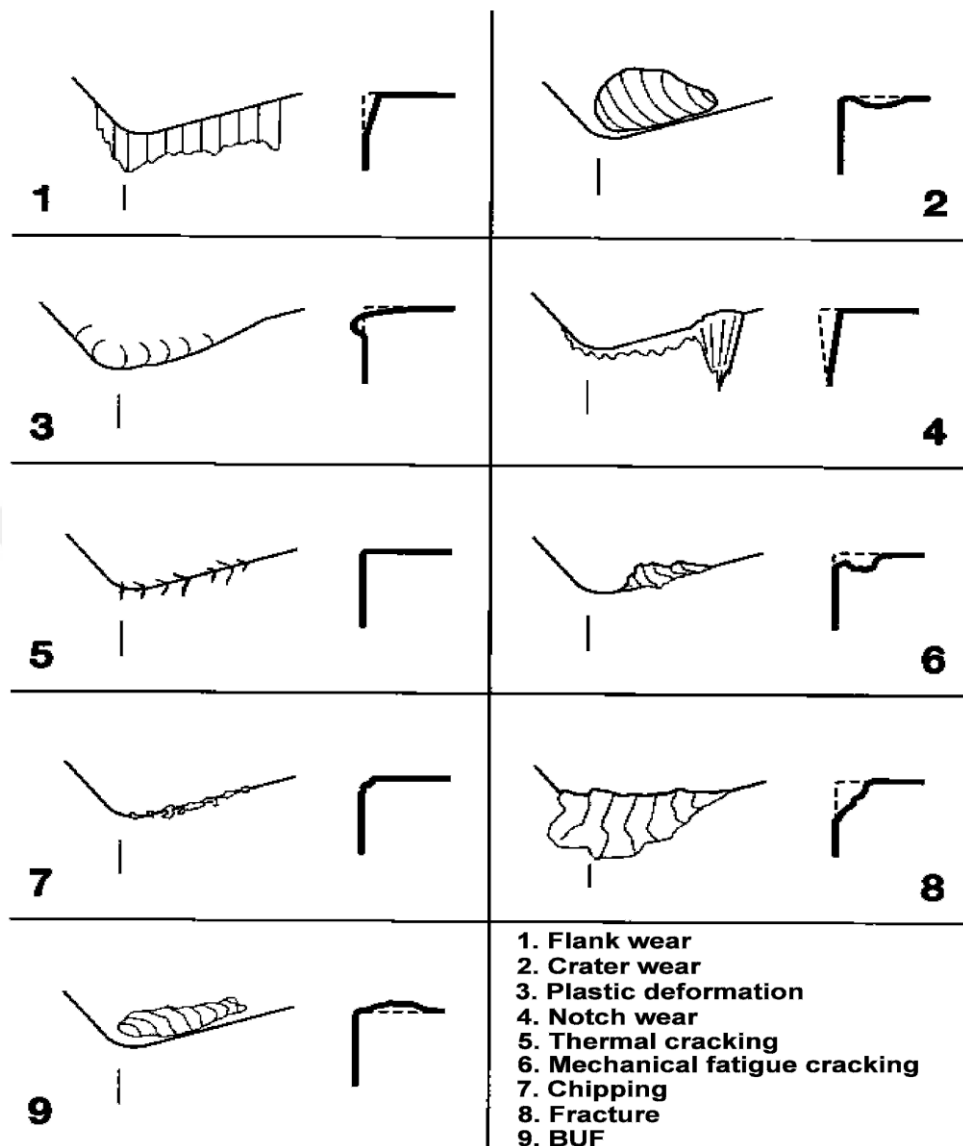


Figure 1.15 Types of wear on cutting tools [21].

Tool wear is a progressive and gradual processes in general. Wear in cutting tools consists of two basic zones: flank wear and crater wear. Depending on the "flank wear", the wear types are divided into four regions.

One of the factors of machinability results and tool life is the choice of cutting angle. The use of rounded and chamfered cutting edges and selection of appropriate cutting angles prolongs the life of the cutting tool.

1.7.4 Surface Quality

As demanded in other materials, copper alloys must have a certain limited value of roughness on the workpiece surface after machining process. For decorative purposes, a smooth and precise surface quality is required. Therefore, surface quality is the most important parameter for evaluating machinability criterion. Surface roughness is a measure of surface quality, usually measured in micrometers.

The peak-stage roughness R_t can theoretically be obtained using the following equation with previously found from the feed f and nose radius:

$$R_{t.th} = r_\epsilon - \sqrt{r_\epsilon^2 - \frac{f^2}{4}} \quad \text{Eq. 1.3}$$

It can be simplified by a Taylor series expansion that gives the following approach:

$$R_{t.th} \approx \frac{f^2}{8.r_\epsilon} \quad \text{Eq. 1.4}$$

Eq. 2 provide to determination of the necessitated feed for a given nose radius, and the expression can be reformulated to give the feed

$$f \approx \sqrt{8.r_\epsilon.R_{t.th}} \quad \text{Eq. 1.5}$$

However, the surface roughness values obtained in practical applications usually deviate significantly from the theoretical value. This can be caused by the following three essential reasons:

- In the machining operations performed with the small feed parameters ($f < 0.1$ mm/rev), wear debris on the cutting edge and radius causes the surface roughness to deviate from the theoretical values.
- During chip removal with higher feed parameters ($f > 0.1$ mm/rev). the growing edge wear of the tools at the nose radius causes deterioration of the quality of the surface roughness.
- There is a range of cutting speeds in which built-up edge (BUE) formation is likely to occur. Periodic breakage of the BUE and displacement of these pieces of BUE often causes a significant deterioration in the quality of the machined surface.

- Built-up edges form when heavily strained workpiece material temporarily deposits on the cutting edge giving the cutting edge an irregular shape. When the BUE breaks periodically, the bits of BUE can then become welded to the chip or the machined workpiece surface [19].

Machinability was assessed by four parameters by evaluating the chip size and morphology and the corresponding cutting tool wear surface, employing the appropriate single point turning technique.

1.8 Background or Problem Statement

The driving force of scientists is to adapt solutions that are sustainable for today's problems in all relevant fields of science. The European Union (EU) has kept on declaring a series of new orders and regulations in terms of climate and environmental aspects. Apart from that, the world health organization (WHO), makes many statements about harm of element lead to the environment and health. It is emphasized that either alternative materials should be used instead of lead or its content should be limited in these declarations.

In terms of economy, machinability is one of the most important factors in industrial scale production. Machining process has a large proportion of share for final manufacture of brass alloys, because many kinds of brass alloys are subjected various cutting process by operator. For that purpose, it has been attracted attention to add alloying elements into brass for improving machinability properties. Lead which is one of alloying elements have been of great interest in this way [28].

Lead, with its low melting and solidification temperature, will fill any micropore during casting. Addition of lead into brass alloys enhances machinability characteristic by behaving as a lubricant on rake surface, resulting in a reduction in cutting force [29]. Moreover, lead also acts as a chip breaker resulting in a good chip disposability. Since lead is low in brass alloy, in the range of between 0.1-3.5 wt.% it precipitates in spherical form at the grain boundaries, causing hot shortness in brass during hot rolling process [30]. However, lead additives in the materials have severe hazards to the environment and human health [31]. Therefore, during material selection and design, engineers must consider safety and health concerns according to the regulations of Restriction of

Hazardous Substance (RoHS) Directives [32]. With regard to drinking water, the international regulations set the upper limit of lead content in water to 0.01 mg/L [26-27].

Lead is a chemical element with symbol Pb (from the Latin plumbum) and atomic number 82. It is a heavy metal that is denser than most common materials. Lead is soft and malleable and has a relatively low melting point. When freshly cut, lead is bluish-white; it tarnishes to a dull gray color when exposed to air. Lead has the highest atomic number of any stable element and three of its isotopes each conclude a major decay chain of heavier elements.

Lead's high density, low melting point, ductility and relative inertness to oxidation make it useful. These properties, combined with its relative abundance and low cost, resulted in its extensive use in construction, plumbing, batteries, bullets and shot, weights, solders, pewters, fusible alloys, white paints, leaded gasoline, and radiation shielding [35].

In the late 19th century, lead's toxicity was recognized, and its use has since been phased out of many applications. Lead is a neurotoxin that accumulates in soft tissues and bones, damages the nervous system, and causes blood disorders. It is particularly problematic in children, in that permanent brain damage may result, even if blood levels are promptly normalized with treatment.

Lead poisoning occurs when lead builds up in the body, often over months or years. Even small amounts of lead can cause serious health problems. Children younger than 6 years are especially vulnerable to lead poisoning, which can severely affect mental and physical development. At very high levels, lead poisoning can be fatal.

Lead-based paint and lead-contaminated dust in older buildings are the most common sources of lead poisoning in children. Other sources include contaminated air, water and soil. Adults who work with batteries, do home renovations or work in auto repair shops also might be exposed to lead. Symptoms of lead poisoning was shown in Figure 1.16.

There is treatment for lead poisoning but taking some simple precautions can help protect you and your family from lead exposure before harm is done [36].

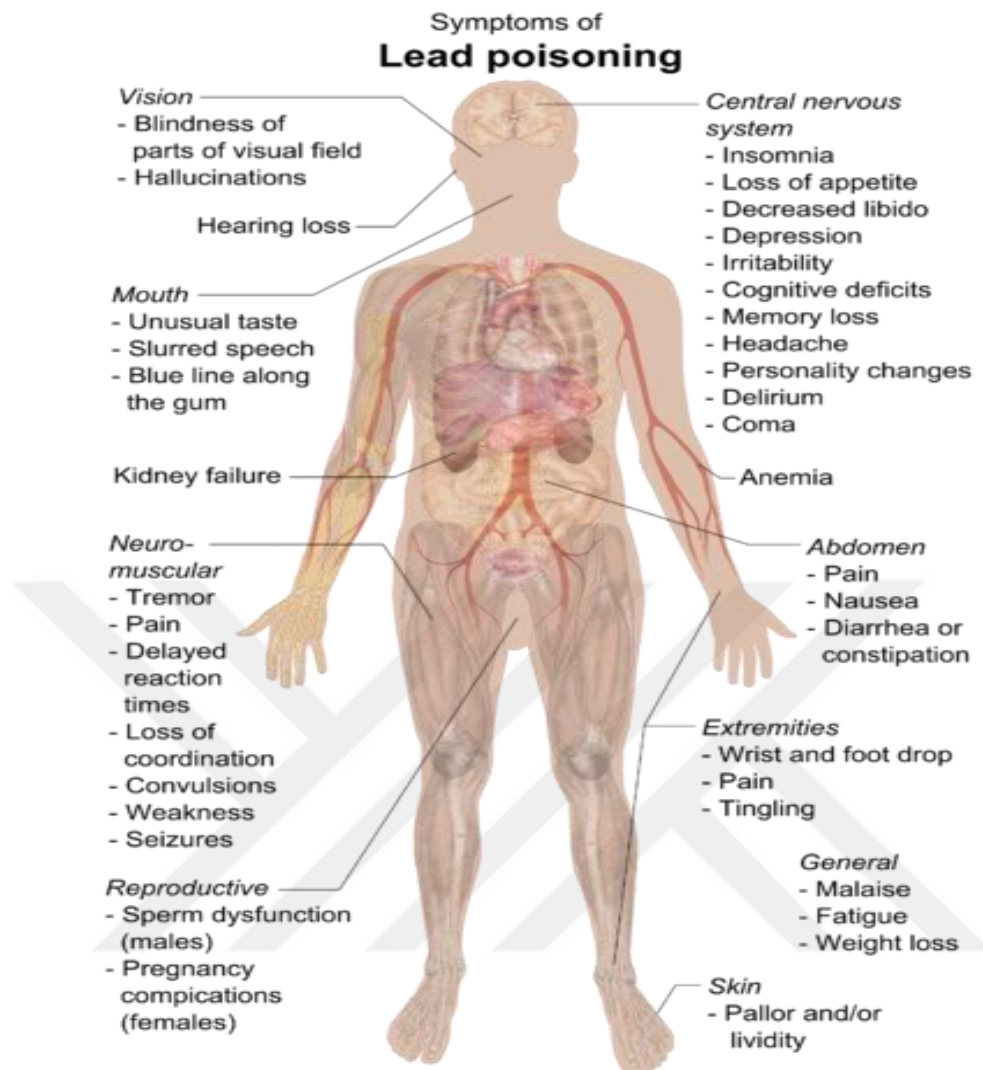


Figure 1.16 Symptoms of lead poisoning [35].

The extraction, production, use, and disposal of lead and its products have caused significant contamination of the Earth's soils and waters. Atmospheric emissions of lead were at their peak during the Industrial Revolution, and the leaded gasoline period in the second half of the twentieth century. Elevated concentrations of lead persist in soils and sediments in post-industrial and urban areas; industrial emissions, including those arising from coal burning, continue in many parts of the world, particularly in the developing countries.

Lead can accumulate in soils, especially those with a high organic content, where it remains for hundreds to thousands of years. It can take the place of other metals in plants and can accumulate on their surfaces, thereby retarding photosynthesis, and preventing their growth or killing them. Contamination of soils and plants then affects

microorganisms and animals. Affected animals have a reduced ability to synthesize red blood cells, which causes anemia [37].

In recent years, there has been various studies related to the lead-free brass alloys in the literature due to the adverse health effects of lead, new regulations and standards that restrict lead contamination to decrease the toxicity.

The element lead can be found in trace amounts in the waste or main parts materials in different areas of the industry as it is naturally found in the environment. Lead content in plumbing parts in contact with drinking water is restricted to use by newly ordered law. Lead-free brass alloys are designed to provide a solution to these changing requirements. These materials should provide resistance to dezincification, stress corrosion cracking and have machinability and forgeability as well as the conventional lead containing brasses.

Short-term exposure to high levels of element lead can cause vomiting, diarrhea, convulsions, coma or even death. However, ongoing exposure to even very small amounts of lead can be harmful, especially to infants and young children. Lead taken in by pregnant women can also pose a danger to the health of unborn children. People may not notice the symptoms of long-term lead exposure, but they are still serious. Anemia is common and lead can also damage the brain and nervous system. Other symptoms are:

- Appetite loss
- Abdominal pain
- Constipation
- Fatigue
- Sleeplessness
- Irritability
- Headache

If a person is continually exposed to lead, as in an industrial setting, it can also affect the kidneys.

Lead exposure is most serious for young children because their growing bodies absorb lead more easily than adults and they are more susceptible to its harmful effects. Even low-level lead exposure may harm the intellectual development, behavior, size and hearing of infants. During pregnancy, especially in the last trimester, lead can diffuse into the placenta and affect the unborn child. Female workers exposed to high levels of lead have more miscarriages and stillbirths [38].

Especially brass and brass alloys containing element lead is widely used in industrial applications in Turkey. In this study, an attempt will be made to produce “lead-free brass” or “green brass” alloys by the addition of alternative metal, alloy and compound additions to examine the effect on microstructure, some properties and machinability.

Pb-free brass under lubricant condition was widely investigated in terms of tribological behavior in other paper. During tribological test, the friction coefficient curve unexpectedly falls in initial stage. The reason one of them is high wear rates in real-time and the other leads to dynamic stability stage by virtue of equilibrium between strain hardening and recovery process. Plastic deformation brings about increasing dislocation movement and void formation in the microstructure. Increasing of two-directional stacking faults is due to the extend and inter-diffuse into each other. Moreover, it is reported that the accumulation of dislocation movement resulted by sliding test leads to change from coarse grains to nano-grains [39].

On account of the aforementioned reason alternative additives instead of element lead for brass alloys will be investigated to improve machinability. The first thing to consider is bismuth element located at the next row in the periodic table. It is effective on chip segmentation [40], but the cost of production increases considerably since it is a rare and expensive element and quantities are limited. Furthermore, it can bring about unsafely intergranular failure in connection with grain boundary segregation [41]. In a study, poisonous and harmful effect of bismuth to human life than lead is discussed and reported [42]. Addition of selenium and bismuth into brass partly improve machinability characteristics, furthermore; structure complexity and higher cost are other disadvantages of these elements participation into brass alloy [43].

Another approach is based on the addition of graphite particles into molten brass. Graphite particle is a common solid lubricant and has an lubricant character [44] which

is available to be used as an additive to brass alloys because it is cheap and environmentally safe [45]. It is very difficult to homogeneously distribute graphite particles in the brass alloy matrix by the casting method due to the density difference of graphite and brass. Therefore, the graphite particles float on the surface of the molten metal [46].

Besides, other elements such as selenium and telluride may be added to the brass alloy in trace amounts for this purpose [47]. However, since the cost of these elements is expensive, it increases the cost of brass production.

One of the widely accepted and adapted idea currently is the addition of silicon element in replacement of the lead [48]. It gives superior mechanical properties such as toughness, elasticity, hardness and workability and provides higher tensile and bending strength [49]. Addition of 2 up to 4.5 wt.% silicon in the brass forms a solid solution and additionally promotes the formation of hard and brittle phases in the brass microstructure that causes to accelerate tool wear and resulting in unfavorable surface roughness.

1.9 Literature Survey

In this part, a literature survey in related studies are briefly presented. The need for more investigation in this subject lies in the fact that generally in many publications their findings seems far away from being a solution for the practical problems which brass manufacturer are facing such as cost of green brass (like in the case of bismuth addition) and reduction in cutting tool life (like in the case of silicon addition).

Vast majority of studies were carried out on commercial leaded brass; however, many research focused and accelerated their attention on the production of lead-free brass by adding alternative alloying additions due to harmful effect of leaded brass on human health recently. For instance; the addition of selenium and graphite to brass alloys as alternative element to replace the lead have been discussed to improve machinability in many papers [22, 34, 39].

Hisashi Imai et. al. has examined characteristics of lead – free P/M Cu60-Zn40 brass alloys with graphite. The addition of 1% graphite has showed good machinability

comparable to that of the practical machinable brass alloys because of the lubricant feature of graphite itself. Sintered brass alloys by SPS technique has a good bonding between brass powders due to the extrusion process applied, their machinability is slightly poorer than that of the conventional sintered and extruded brasses [45].

In an extended project, the same researchers investigated mechanical properties and machinability of extruded Cu-40 % Zn brass alloys with bismuth via powder metallurgy process. One of the results of that study is improvement of cutting and drilling ability by addition of bismuth. Chip formation of extruded brass alloy with addition of bismuth is semi- continuous chip type. Primary particle additive precipitated at grain boundary has caused to decrease in elongation. [51].

Hidekazu Sueyoshi et. al. examined machinability of copper sulphide – dispersed lead – free bronze. In that study, bronze with dispersed copper disulfide has been produced by adding MoS₂ to molten bronze at 1200 °C temperature. The dispersion of Cu₂S reduces the coefficient of friction on the rake surface and increases the shear angle, resulting in a decrease in cutting force. The Cu₂S dispersed into bronze has a good chip disposability because Cu₂S acts as a chip breaker [52]. Extended investigation with same researchers has addressed the influence of zinc sulphide ratio in the lead-free bronze on the machinability. The machinability has been improved with decrement of the zinc sulphide ratio. The zinc sulphide can be formed with copper sulphide at elevated temperature, at which the zinc sulphide has been unstable according to thermodynamic calculation. The ratio of zinc sulphide has increased with increasing amount of zinc in bronze casting. Tin does not affect the zinc sulphide ratio when the tin content is less than about 4 % mass [53].

M.A. Taha et. al. has studied on evaluating the machinability of Pb-free brasses with Si from 1% up to 4wt% content. With the silicon content increasing from 1% to 4wt%, the tool wear has increased by 140%, machined surface roughness is higher 25%, while type of chip form has changed from continuous to discontinuous, and also cutting force has decreased by 50%. The result of machinability are correlated with the alloy's mechanical properties and with the phases present in the microstructure [54].

Shufeng Li et. al. has studied the effect of Ti addition on mechanical and machining characteristic for Cu40Zn lead -free brass prepared by powder metallurgy. It has been reported that Cu₂ZnTi intermetallic compound (IMC) formed by reaction between Ti and Cu-Zn. That case has significant grain refining effect on extruded Cu40Zn brass. The strength of the prepared alloys increasing due to precipitation hardening and deformation process has been observed [55]. In another study of the same authors; Ti combination with Bi has been led to intermetallic compound which improved mechanical and machinability properties by virtue of the reaction between Bi and Ti at elevated temperature [56].

The other study conducted by Ima et. al. focused on examination of machinability characteristics and microstructure for leaded brass. The examination has based on microstructure and cutting force behavior which has been emphasized on improving machinability properties due to having the fine globular size lead particles and its homogenously distribution in the microstructure [57].

Toufatzis et. al. has performed a study in which comparing machinability features between leaded brass (CW614N) and lead-free brasses (CW510L, CW511L, and C27450) including dual phases (alpha and beta) from the standpoint of power consumption and chip formation. The machinability has been also related with mechanical properties and phase composition. The results of the study have showed that the chip size and morphology are mainly affected to machinability of leaded brasses, which depends on the microstructural distribution of lead particles and β -phase intermetallic fractions. Whereas, the- β -phase fractions containing lead-free brass alloys have a great effect upon constitutes of micro crack and formation of shear band [58].

H. Ima et al conducted a project and reported in terms of mechanical and machinability properties by adding chromium and graphite particles to brass alloy. The consolidation of powder has been carried out by spark sintering plasma process. Drilling test under dry condition has been used for evaluation of machinability for lead-free brass alloys. The chromium carbide taken place after heat treatment has brought about inhibiting machinability properties due to decreasing graphite particle content [59]. Another study by the same researchers reported that the increase in density and improvement of the

microstructure for the sintered billet was achieved by hot extrusion. Alloying elements with super saturated solution which act as grain refinement has precipitated with nano/micro scale in matrix after hot extruder process; thus, it was enhanced mechanical properties [60].

Schultheiss et al. has carried out a study which assessed machinability properties in comparison with between leaded and lead-free brass during turning operations. The evaluation of machinability is based on three categorized parameters such as surface roughness, power consumption and chip morphology. Silicon (Si) replaced with element lead in brass microstructure has exhibited improvement of mechanical properties when comparing to leaded brass, however; the machinability features of leaded brass superior or better than lead-free brass [61].

In the other study, the effect of tin addition into Cu70-Zn30 brass alloy on microstructure and machinability has been investigated. The increment of tin amount in brass microstructure have led to shift towards peritectic reaction through lower zinc content in Cu-Zn binary diagram and also suppressed the formation of α - phase and contributed the formation of β - phase in the Cu70-Zn30 brass alloy and thus transformation is taken place from single alpha brass to duplex ($\alpha + \beta$ phases) brass alloy. Increasing tin additives in brass microstructure has reduced surface roughness and machining force (F_m) [62].

Koboyashi et. al. has studied on investigation of tribological properties for sulfide-dispersed bronze. Wear test including determination of wear rate and friction coefficient parameter were performed under dry condition. The result of study was reported that seizure and scoring had been reduced by sulfur dispersion in the bronze, like as Pb in the Pb-bronze [63].

In a study of Yang et. al., the addition of silicon and aluminum additives into brass matrix has altered a phase composition in Cu-Zn diagram according to zinc equivalent (given information detail in section 3.7) and has changed the morphology of the phases formed in the microstructure. Besides, ultrafine intermetallic compounds have been found at the grain boundaries of the α and β interfaces. The microhardness of brass alloys and accompanied by ultimate strength of them has increased with increasing zinc equivalent

value. Conversely, elongation of them has decreased with increasing zinc equivalent value [64].

In the study of Atsumi and their colleagues, 1-3 wt. % bismuth and trace amounts of iron, tin and chromium added into brass alloys were produced by casting method. Irregular bismuth particles were precipitated around the alpha phase and the high fraction of the beta phase with fine intermetallic compounds was found in the microstructure. The average yield and ultimate tensile strength have increased with increasing hard beta phase fraction [65].

In the other study, CW511L (CuZn38As) lead-free brass produced by different casting technology that was compared in terms of microstructure, mechanical properties and corrosion resistance. The result of microstructural analysis was indicated that various phase composition and morphology which occurred in microstructure from different solidification rate and additives has affected on strength and hardness values of samples. The research focused on the quality of castings production rather than the effect of alloying elements. It has been reported that the addition of 0 to 1.2 wt. % aluminum and tin lead a significant effect for the solution of dezincification tendency in the brass matrix. In addition, 0.033 wt. % of arsenic has been found to have a greater effect on the tendency for dezincification than tin and aluminum. However, as the arsenic content has been increased further, corrosion could only take place on the surface of the samples [66].

In a study of Adegbenjo et. al, Mn was used as additives instead of lead for a cartridge brass with Fe and Ni impurities, tensile strength was found to be increased at low annealing temperature [67]. In further study, silicon was used as additives in brass composition instead of lead. The result of experimental analysis indicated an improvement in tensile properties in all annealing conditions which were selected in experiment studies[68].

F. A. Ovat, L. et. al. conducted a study on the effects of mechanical properties in brass by adding different proportions of Mn and Al additives. The optimum levels of tensile strength, hardness and impact values of brass was achieved in aluminum and manganese ratio between 2 – 5 wt. % [69].

The addition of Mn into brass using as grain refinement agent and also improving mechanical properties of samples have been reported in the study of of Bondan Tiara

Sofyan. Sample alloys have been produced by gravity casting method and homogenization process has been performed at about 800 °C for 2 hours. Microstructural examination revealed that an increase of beta phase formation and of Mn rich intermetallic compound precipitated at grain boundaries with increasing addition of Mn additives into brass. It was emphasized that this intermetallic phase led to decrease of elongation of brass due to precipitation along the grain boundary with both smaller and larger size phase formation.

In another study, they have also conducted an investigation on the deformation properties of Cu-29Zn alloy. The experimental process was the same above and the samples were subjected to different deformation conditions. Cold-rolling process with the deformation rate of 20, 40, and 70 % applied for all samples. It was observed that slip band density reduced with increasing Mn addition at 20% deformation rate. When the deformation level increased to 40%, twinning became the dominant mechanism in contradict to in 20% deformation. Twinning density slowly rose due to the existence of Mn. At the rate of 70% deformation, shear bands were observed and led to flatten the β' phase. Mn content had positive effect on the stimulation of more shear band [70].

A. S. Paipetis et al. examined the machinability of lead - free brass alloys with increasing beta phase which resulted in significant improvements in the microstructure. The increment of beta phase in the microstructure of brass could cause embrittlement; thus, the process was performed in taking into account the mechanical properties of EN standards. There was various heat treatment in order to alter the microstructure and diversify mechanical properties of lead-free brass alloys. Appropriate heat treatment was selected to investigate the effect of β -phase augmentation on microstructure and mechanical properties. The increase of β -phase after heat treatment has concluded in reduction in elongation owing to grain coarsening; moreover, formation of brittle microstructure by not corresponding to EN 12164 and ASTM B927 standards [71].

Li et. al. examined the adhesion behavior of aluminum bronze on the tool tip during turning. Adhesion depends on the material which tool tip is made of. The adhesion was found more intense and more severe in HSS than cemented carbide tool. The thickness depth of adhesion was significantly affected by temperature distribution on the tool surface [72].

Additives such as silicon and bismuth to produce green brass by replacing the lead in the brass totally or partially both of which can only offer limited solution and their contribution is limited in similar machinability of the brass, however they do not provide comprehensive or satisfactory solutions in finding cost effective alternative additive elements for health problems and as well as to increase the cutting tool life.

That paper was based on the effect of chemical composition and hardness value on machinability parameter. From the standpoint of cutting force, commercial alloy is lower than pure alloy in ternary systems. They have exhibited similar behavior for depth of cut and feed values in some conditions. The type of alloying element present and its content has substantially influenced the cutting forces. Brass alloys including tin content have the lowest values in terms of cutting and feed forces by virtue of presence beta prime and gamma phases. In contradict, the effect of aluminum increases cutting force with rising aluminum content because of domination of beta phase in entire microstructure [73].

Table 1.1 is shown the effects of alloying elements on mechanical and machinability for brass alloys in previous literature studies in a graded manner. Moreover, this table points out to the studies lacking in the literature with these alloying elements.

Table 1.1 Summary of the effects of additives on the properties of brass alloys

Additives/ Property	Chip Formation	Surface Roughness	Tool Life	Hardness	Elongation	Tensile Strength
Sn	+++	++	Not studied yet	+++	+	+++
Bi	+++	+++	+++	+++	+++	+++
Al	+++	++	Not studied yet	++	+++	++++
As	++	+++	++	++	++	++
Si	++++	++	+	++++	+	++++
Graphite	+++	+++	+++++	+	+++	+++
Lead	+++++	+++	+++++	++	+++	++++

+: Poor ++: Moderate +++: Good ++++: Very Good +++++: Excellent

1.10 Aim of Thesis

The aim of this thesis is to produce and characterize of a new generation lead-free brass or green brass to substitute commonly used leaded brass in industry. In previous studies, lead free brass produced cannot be adapted to apply industrial-scale production; in addition, lead -free brass alloys currently used accelerate tool wear. The following question arises from this point and the current study was conducted to seek answers to this question.

“Why are different additives needed instead of lead in brass alloys?”

Important considerations and facts about lead brass are given below.

- Leaded brass (free-cutting brass) materials are produced by casting process as final products for various applications such as plumping devices, lock parts, watches and faucet material. Leaching of lead into potable water in lead added brass alloys used as plumbing components and faucet materials can be considered as seriously hazardous to human health. Since lead is a heavy and toxic metal. This case impetus to govern new stricter regulations from The World Health Organization (WHO) to limit lead solution under 10 mg/L in drinking water. According to NSF/ANSI 61 standard, the use of lead as additives into brass and bronze alloys is restricted to under the level of 0.25 wt.% due to the harmful effect of human health and environment.
- Chip can be occurred within fine sizes during machining of leaded brass alloys. Chips of leaded brass with fine size during machining which release to air, brings about the respiratory tract infections such as bronchitis and asthma by inhalation. Chip of leaded brass with fine size can also trigger cancerous disease by time apart from the above diseases.
- Brass materials are widely used because of readily plastic deformation ability, durability, and resemblance to gold in decorative applications and jewelry fields. Brass material chips are generated during machining processes to get the final product. When the chip sizes of the leaded brass materials are compared with the chip sizes of the other metallic materials, the leaded brass materials have smaller chips. These small chip particles penetrate into the mechanical and electrical components of the lathe, rendering them dysfunctional further by time.

2 MATERIALS AND METHOD

Although leaded brass alloys are widely used, usage of them is indispensable in parts like as faucet, water pipe, hydrometer block in plumping system in the industry. It can be found as a final product with commercial quality in the market via machining process performed after casting. Lead free brass alloys produced in previous studies and in the industrial environment cannot fulfill all the properties of leaded brass alloys.

Determination for the selection of additives improving machinability of brass alloys is discussed under the title of "Consideration for selective of additives" which emphasizes in terms of thermodynamic, thermal expansion and toxicity properties.

In previous literature studies, bismuth, graphite, tellurium, selenium, and silicon were tried as alternative alloying elements instead of lead. Brass with bismuth is not preferred in the industry due to both the uncertainty of its toxicity and its rare element. The studies of brass alloy with graphite have limited because a brass alloy produced by casting method hardly due to the difference in density. Tellurium and selenium are expensive alloying elements because of being rare elements. They are not appropriate for commercial applicability as they are not able to use alone as additives. It can be used as additives with either graphite or bismuth. Among these alloy additions, only silicon-added brass alloys are used commercially on an industrial scale, however; the biggest obstacle of the alloy produced with silicon is the shortening of tool life due to high tool wear rate.

Selected alloy additives were employed to produce lead-free brass by the casting process, and then their machinability in terms of chip formation was studied. Promising samples with respect to the machinability were characterized by mechanical, wear and corrosion tests. As can be seen in Figure 2.1, a flow chart was designed for experimental studies.

In this section, experimental studies and material selection are categorized under 9 main subheadings. These are as follows: Consideration for Selective of Additives, Experimental Equipment, Casting Procedure, Metallographic Studies, Corrosion Studies, Machinability Test, Surface Roughness Measurements, Mechanical Test, Wear Test.

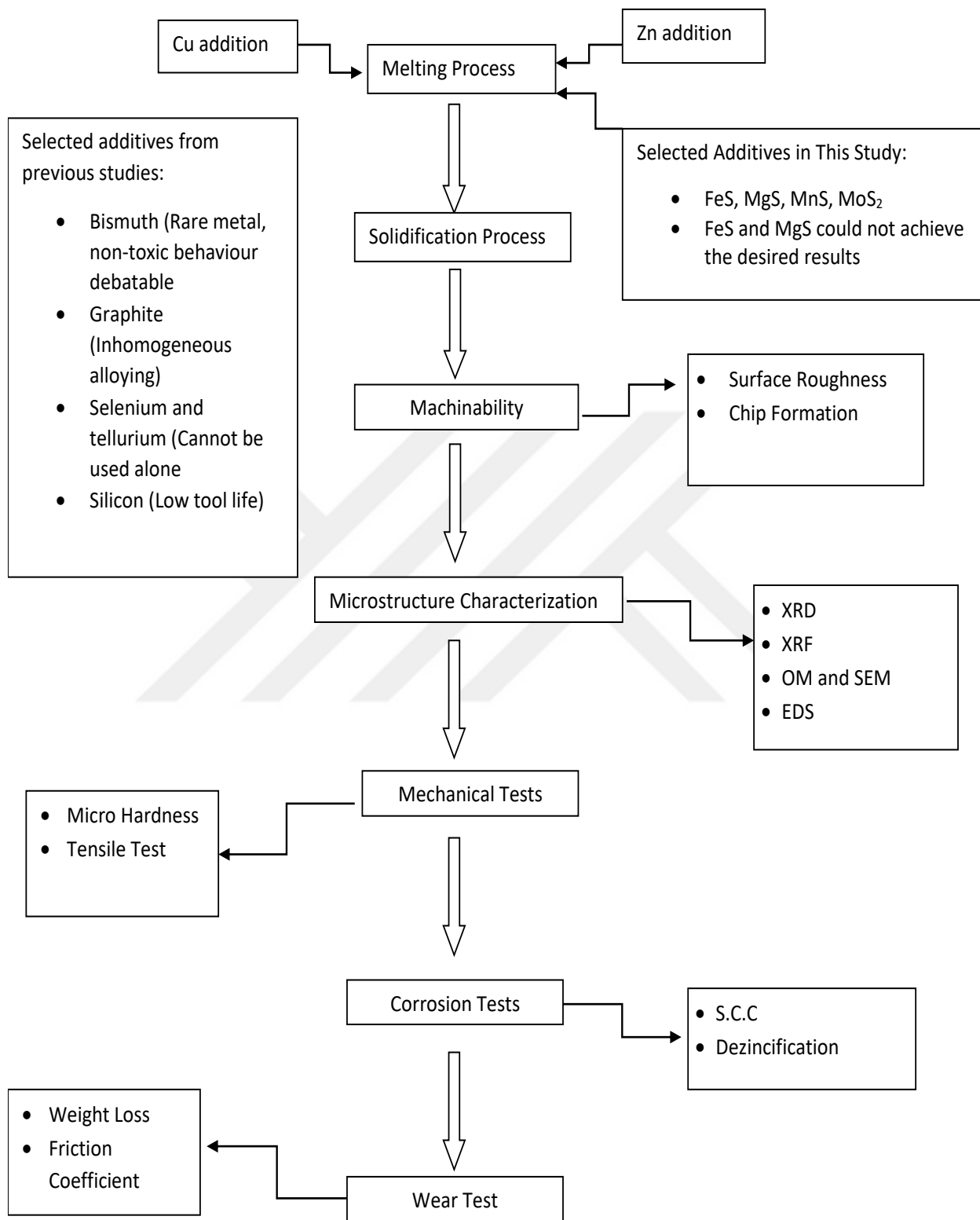


Figure 2.1 Flow Chart of Experimental Studies

2.1 Consideration for Selective of Additives

The selection of additives which facilitate machinability based on some characteristics of sulphide inclusions by considering the fact that they promote machinability of metal and non-metal materials. During machinability of metallic materials, the presence of-metallic inclusions to assist for easily removal of chips from working materials. The study of Kiessling [74] presents below several promising criteria to explain this situation.

- The inclusions cause crack propagation, and act as a stress riser in shear plane forming an embrittled chips which can be easily broken during machining.
- The homogeneous distribution of inclusions in the microstructure leads to reduce tool wear parameter due to the low plastic deformation, besides they provide to easily flow of machining part on workpiece.
- Due to their lubricant properties they alleviate an abrasive wear from flank face of a cutting tool

The type of additive for improving machinability in brass alloys has been selected to take advantage of the similar sulfur based/compound additives to enhance machinability of steel.

During the machinability of the workpiece, the ambient temperature between the workpiece and cutting tools can reach 750-800 °C, resulting in a large-scale thermal gradient [75]. Steel matrix and non-metallic inclusions having different thermal expansion coefficient brings about increase in stress or tension fields in microstructure due to the existence of thermal gradient and thermal expansion mismatch. The similarity of thermal expansions will have no effect on the steel matrix. However, when the thermal expansion of the steel is greater than the inclusion, and vice versa, it will create stress raiser fields in interface regions and trigger the nucleation of the cracks that will cause fracture during machinability. The intensities of stress fields which depend largely on size and numbers of the presence inclusions pave the way for nucleation or propagation of cracks in microstructure. [73-74]. The effects of non-metallic inclusions on the steel matrix is demonstrated in Figure 2.2

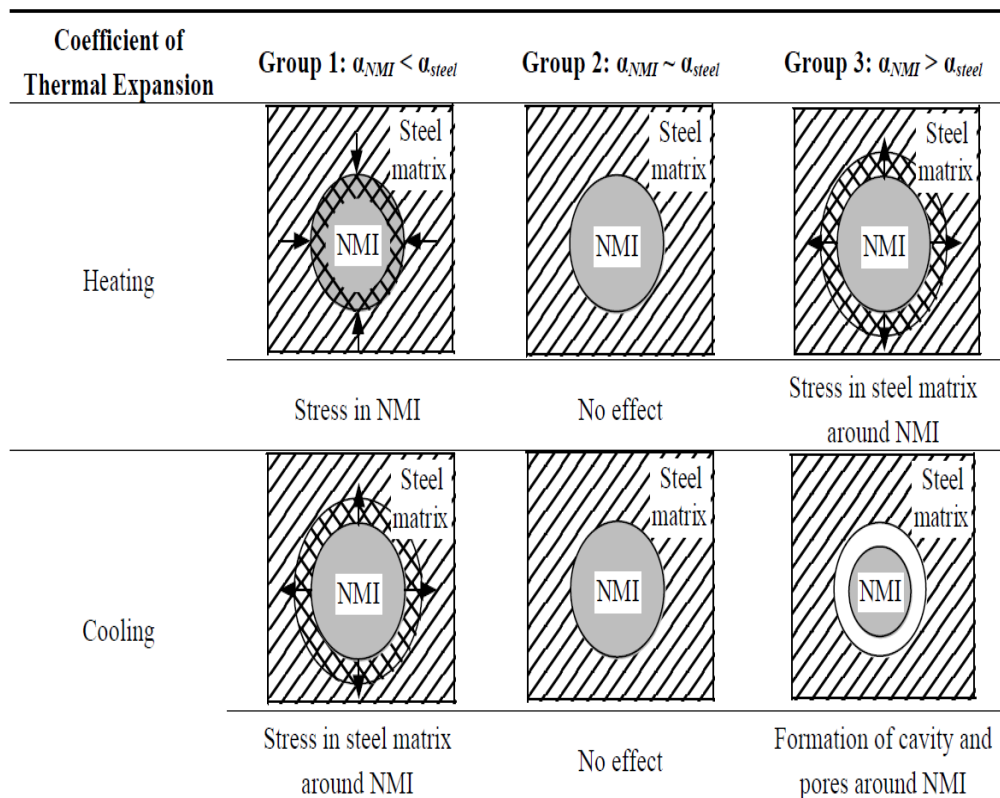


Figure 2.2 The effects of non-metallic inclusions on the steel matrix (NMI=Nonmetallic inclusion) [77]

In previous studies, thermal expansion values of inclusion based additives and their effects on steel matrix in some non-metal inclusions with sulfides form were examined and presented in Figure 2.3. [77]. Another study emphasized that the value of thermal expansion coefficient had been influenced by the chemical composition of the steel matrix. Therefore, the effect of inclusion on steel matrix can be varied with the steel grade [5]. As can be seen in the figure, the greater the difference between the coefficient of steel and non-metallic inclusions, the greater the magnitude and probability of creating stress. These values should be taken into consideration while additives are employed for alloying to improve machinability without inhibition of their mechanical properties and corrosion properties.

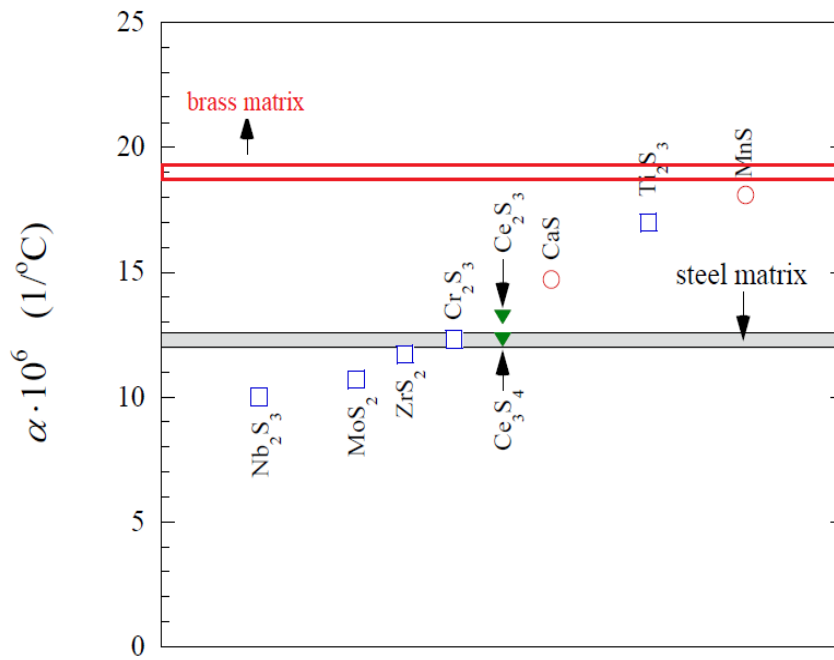


Figure 2.3 Thermal expansion coefficients of non-metallic inclusions [77]

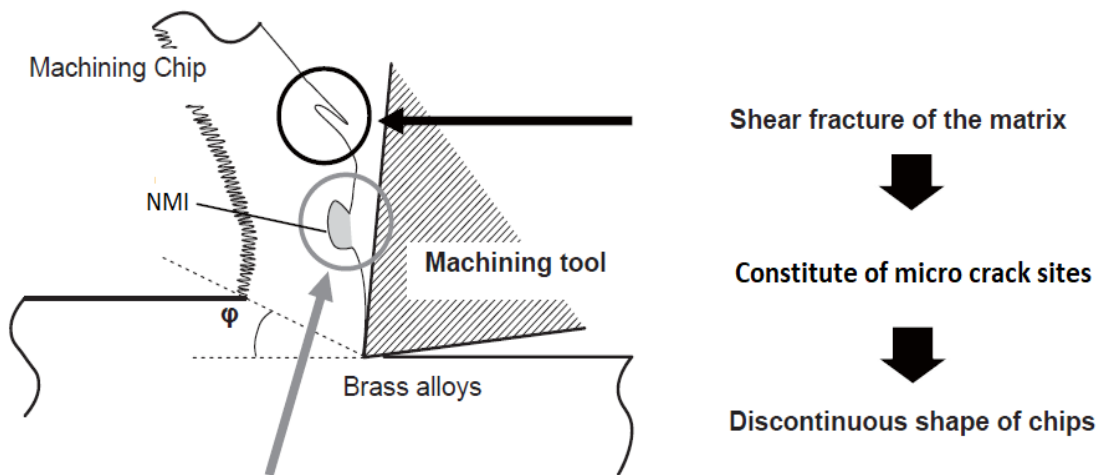


Figure 2.4 Model of machining mechanism for brass alloys with NMI [43]

Most of these sulphide inclusions, which are insoluble in brass matrix as in steel matrix, precipitates at grain boundaries or alpha/beta interface like lead element in F.C.B matrix; thus, leading to micro crack sites. These micro cracks result in shear fracture during machining process, leading to discontinuous chip formation. Figure 2.4 shows schematically the role of NMI in the process of machinability. Sulphide inclusions that

precipitate in steel matrix give rise to decreases in shear strength in cutting zone. Moreover, they are sources of stress fields due to having various hardness values (most of them are lower than steel matrix). Inclusions which have distorting effect on the matrix is formed with holes or cracks, which makes the steel weaker and also, they act as internal notches because of their low hardness. These notches cause easy chip breakage [78]. They can cause a high rate of deformation within local zones of steel matrix during machining. For example, the addition of MnS in steel improve the machinability, because they are soft in comparison to steel matrix; furthermore, they act as a void. Hence, they separate from the surrounding steel when the chip is formed by the action of the cutting zone. As a result, the chips are shorter in length which promotes easy removal. There exists lower friction between the tool and chip, which decreases the total power consumption during machining. Since the chips are removed at shorter lengths with lower friction coefficient, the surface finish of the component will also be superior for the sulfur containing steels compared to the other steel [79]. The deformation of MnS inclusions in steel increases the area of interface region between inclusion and the steel matrix. This can lead to reduction in mechanical performance properties of steel through a decrement in plasticity and toughness. Furthermore, they accelerate the risk of pitting corrosion due to acting as initiation sites. [80], [81]

To produce a solubility of Metal Sulfide (MS) products in brass matrix requires to know relationship the activity of the sulfide and the activity coefficients of the elements in solution. Previous study highlights the importance of that point [82]. The activity coefficients of the elements in brass matrix is taken not depending on concentration and the activity of the sulfide is taken as unity and below equations follows help to understand mechanism of solubility product for MS.

$$\text{MS}_s = \text{M} + \text{S} \quad \text{Eq 2.1}$$

$$\text{Ksp} = C_M^{\text{resid}} \times C_S^{\text{resid}} \quad \text{Eq 2.2}$$

$$C_M^{\text{resid}} = C_M^0 - C_M^{\text{MS}} \quad \text{Eq 2.3}$$

$$C_S^{\text{resid}} = C_S^0 - C_S^{\text{MS}} \quad \text{Eq 2.4}$$

Ksp: Solubility product

C_M^{resid} : Concentration of reactive element in wt. %

C_M^0 : Total reactive element content of the alloy

C_M^{MS} : Amount of reactive element tied up in the sulfide.

C_S^0 : Total sulfur content of the alloy

C_S^{MS} : Amount of sulfur tied up in the sulfide.

The solubility product constant, K_{sp} , is the equilibrium constant for a solid substance dissolving in an aqueous solution. It represents the level at which a solute dissolves in solution. The more soluble a substance is, the higher the K_{sp} value it has. Figure 2.5 shows the variation of solubility product of sulfide depends on residual sulfur content in solution.

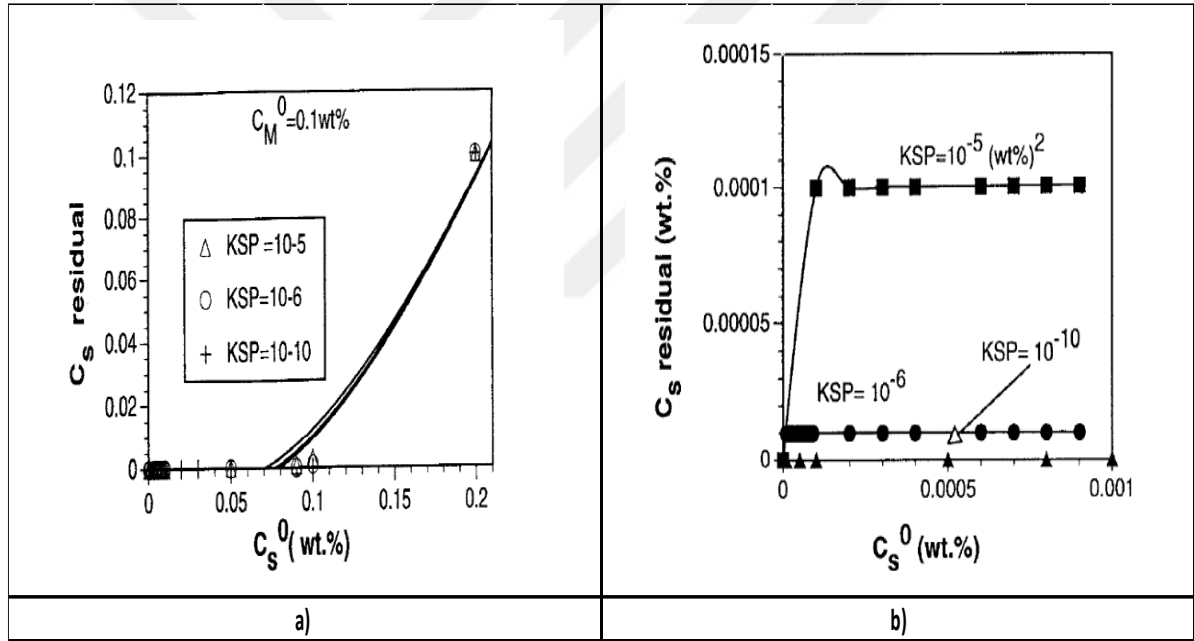


Figure 2.5 Variation of solubility product of sulfur depending on residual sulfur concentration in solution a) higher values of C_S^0 and b) lower values of C_S^0 [82]

A previous study highlights the importance of three points:

1. The residual sulfur content decreases with the amount of reactive element added
2. The residual sulfur content decreases with increased stability of MS i.e a decrease in K_{sp}
3. The residual sulfur content is essentially independent of the initial sulfur content between two critical values of C_S^0

The two critical values of C_S^0 mentioned in 3 are a low value, below which the sulfur activity is too low to form sulphide, and high value which there is more than the stoichiometric amount of sulfur to react with all the reactive element present [82].

Figure 2.6 shows the sulfide forms of some metals on the Ellingham diagram. Another important point in the selection of additives for alloying is their high temperature stability. The changes in the composition of the additives from high temperature reaction after casting could affect the brass matrix unexpectedly. Ellingham diagram was used for the determination of their stability at high temperature which is shown in the graph and the equilibrium region for reduction of metal oxides and sulfides depending on temperature.

Apart from these factors, the selection of additives should be considered in terms of their economic value and availability of the candidate material. In this study, selected additions for brass alloys was inspired by previous studies on steel. MoS_2 , MnS , FeS and MgS were selected to use as additives for improving machinability of brass. In the experimental studies, samples prepared by FeS and MgS additives have not been included in this chapter because they could not reach expected results in terms of chip formation. Figure 2.7 shows the chip formation of samples prepared with MgS and FeS together with reference samples. It is also emphasized in the relevant references that the selected MnS and MoS_2 additions do not have a significant toxicity for MnS , and that MoS_2 have not exhibited toxic properties.[83], [84]

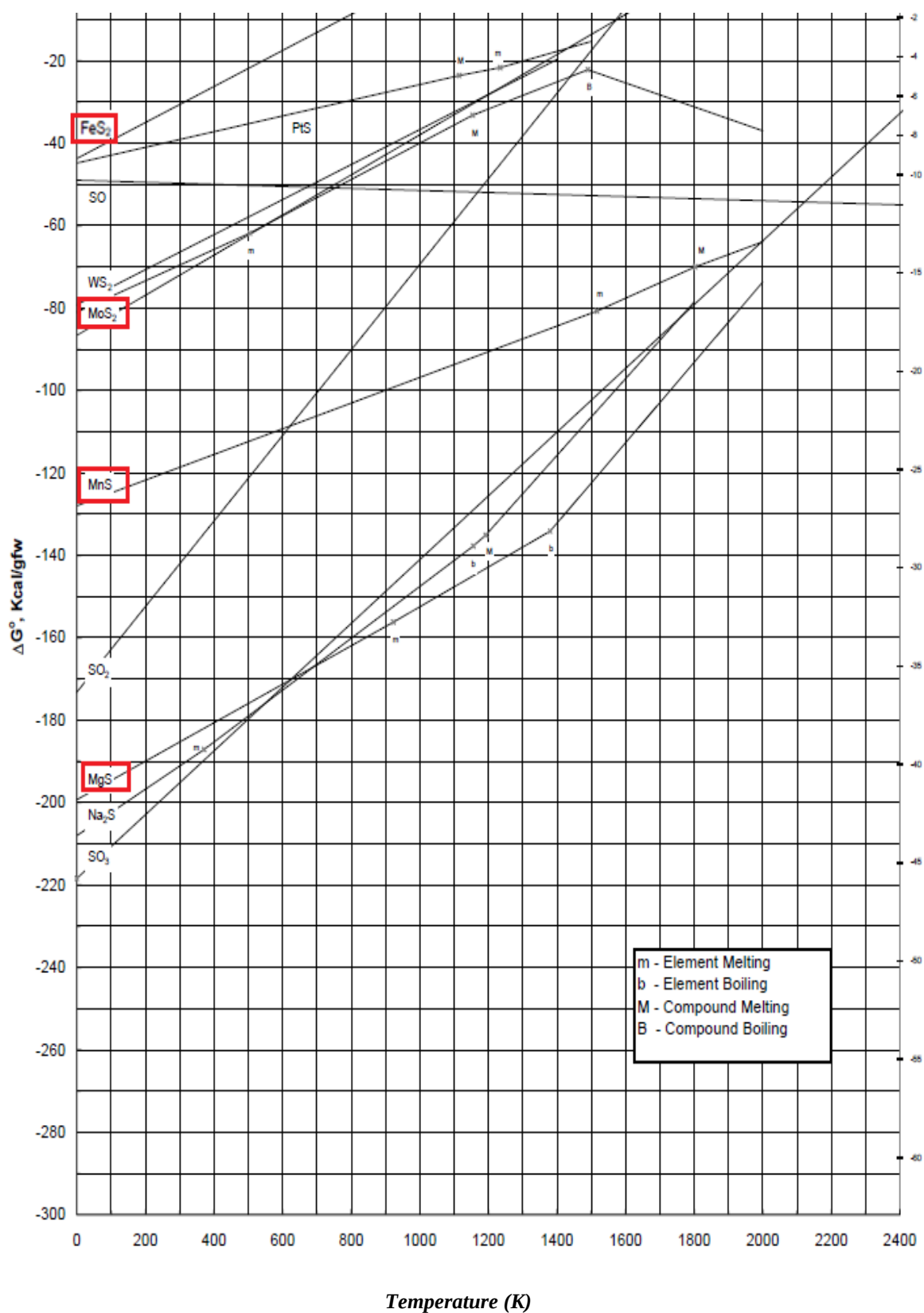


Figure 2.6 Ellingham diagram for sulfide forms of some metals [85].

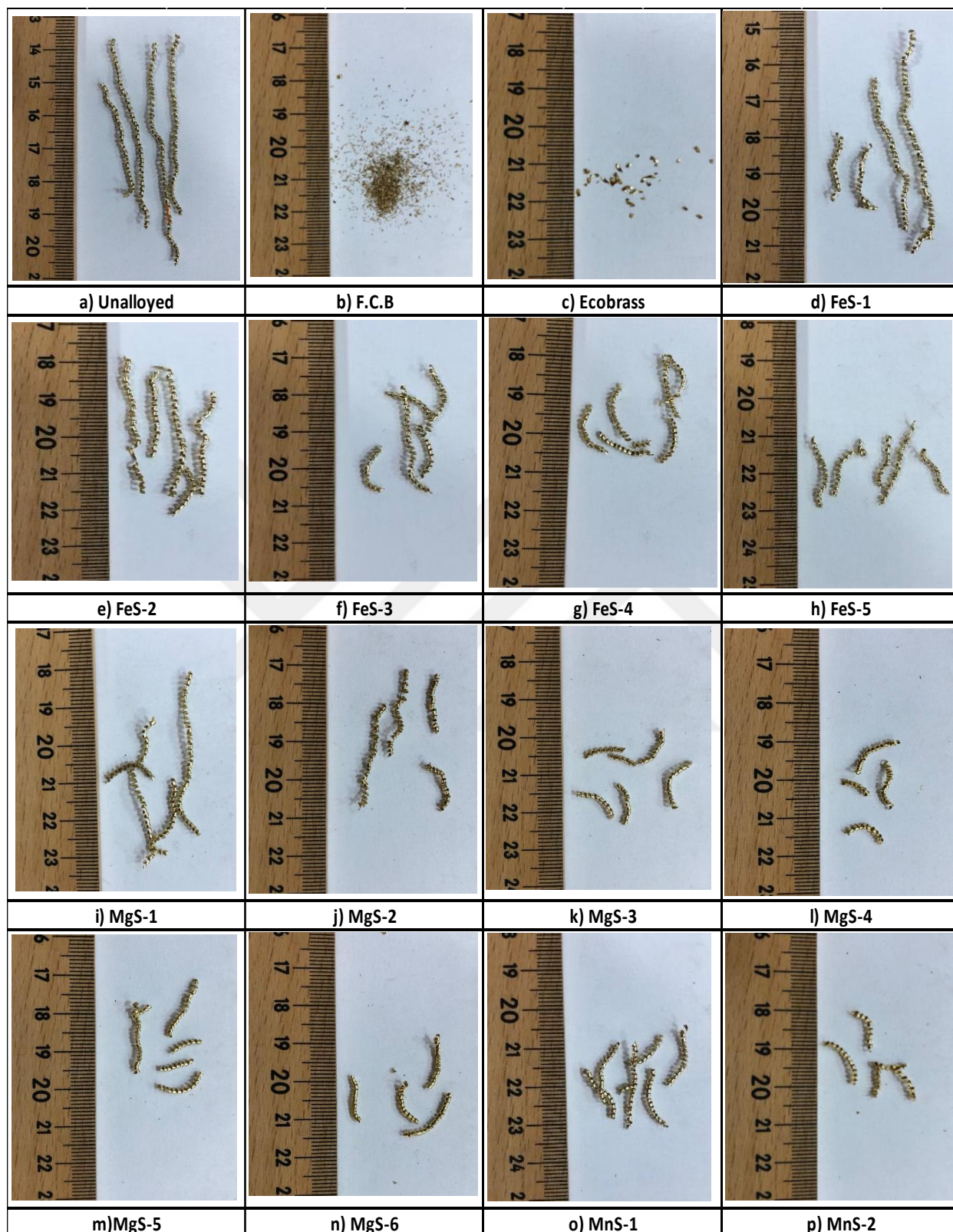


Figure 2.7 After machinability test, chip formation of a) Unalloyed, b) F.C.B, c) Ecobrass, d) FeS-1, e) FeS-2, f) FeS-3, g) FeS-4, h) FeS-5, i) MgS-1, j) MgS-2, k) MgS-3, l) MgS-4, m) MgS-5, n) MgS-6 o) MnS-1, p) MnS-2

2.2 Experimental Equipment

In experimental studies, the following equipment and devices were employed for the production and characterization of samples; induction furnace, precision balance, graphite crucible, optical microscope, scanning electron microscope, X-ray diffractometer, X-ray fluorescence, microhardness measurement test device, potentiostat, were used and facilitated in this thesis.

2.2.1 Induction Furnace

Melting processes for brass alloy samples were carried out in an induction furnace (supplied from Agentia Inc.) which was shown in Figure 2.8. There are wide application areas for induction furnace from jewelry sector to cast iron and steel production due to having effective stirring feature with the use of electromagnetic field. The real temperature can be measured up to 1300 °C with a thermocouple which is located in the side of crucible by drilling a hole.

Technical data of induction furnace used in this study was shown in Table 2.1. The amount of alloy elements was adjusted using digital scale and charged into graphite crucible to melt prepared alloys via induction furnace.

The graphite crucible, which can stand against high temperature, is used as a container for metal melting. The capacity of crucible is 300 cm³

Chiller was integrated into the induction furnace to remove excess heat on the copper coil and the furnace's electrical parts by means of circulation water. Chiller was purchased from Gazi Soğutma Inc.

Table 2.1 Features of Induction Furnace used for melting process

Rated voltage	400 (50) Hz
Rated power	10 kW
Max. Operating temperature	1500 °C
Crucible capacity	300 cm ³ (bulk charge melting)
	280 cm ³ (granulated charge)



Figure 2.8 Induction furnace system used in the casting process

2.2.2 Scanning Electron Microscope (SEM) and Chemical Analysis (EDS)

FEI Sirion Scanning Electron Microscope (SEM) was used to investigate microstructure and fractured surface of samples which was shown in Figure 2.9. SEM equipped with Energy Dispersive Spectroscopy (EDS) was used to analyze on cast samples to get information about morphology and to determine elemental distribution. Analysis were conducted using Backscatter electron detector integrated to SEM to distinguish phase composition on microstructure and to get images at different directions and different magnifications.

The chemical compositions of samples were determined using the Thermo Scientific Niton XL2 Analyzer instrument which was shown in Table 2.3. When X-ray fluorescence (XRF) spectroscopy and energy dispersive spectrometry chemical analysis is compared, the results of the analysis do not appear to be the same. The measurement of the XRF reflected chemical composition of the entire sample; on the other hand, the measurement of the energy dispersive spectrometry provides only a small fraction of the microstructure in chemical composition.



Figure 2.9 Scanning Electron Microscope for microstructure analysis

2.2.3 X-Ray Diffraction Analysis (XRD)

Phase composition of all samples were identified by using X-Ray Diffraction (XRD) analysis technique. Firstly, all samples were cut in an appropriate dimension to place in sample holder and then the voltage was adjusted 40 kV and the current was selected 40mA for XRD analysis. All prepared samples and reference samples were scanned from 20 to 80 in two theta angle with the scan rate of 2° min^{-1} in order to identify phase composition. X'Pert Highscore Plus software was used to determine the phase composition of all samples. Bruker AXS D8 Advance X-Ray analysis instrument was shown in Figure 2.10.



Figure 2.10 X-ray diffraction instrument for phase detection

2.2.4 X-Ray Fluorescence Spectroscopy (XRF)

The energy dispersive X-ray fluorescence spectroscopy (XRF) is one of the methods to determine elemental composition of materials with qualitative and quantitative manner. It is useful for the control of the chemical analysis of equipment parts by virtue of being a non-destructive technique in industrial applications, nowadays.

The specimen is exposed to primary X-radiation having energetic photon to extract electron from inner shell. While electrons spinned from outershell drops into inner shell to preserve orbital shell energy, fluorescence radiation is emitted with a particular energy for each material. Scattered fluorescence radiation reaching detector translated to data on the computer. Thermo Scientific Niton XL2 Analyzer instrument was employed in this study which was shown in Fig.2.11.

XRF devices have the many advantages as following:

- X-radiation has absolutely no permanent effect or damage on the material and also completely protects the quality, thus used as a non-destructive techniques
- Sample preparation for XRF analysis is very simple and measurement time is short and ready in seconds
- No chemicals are used
- X-radiation is a method which does not use hazardous chemical materials thus there is no risk for operator.



Figure 2.11 The Portable XRF Spectrometry for determination of chemical composition

2.3 Casting Procedure

Casting process for brass alloy production consists of two stages:

First stage: Brass contains copper and zinc is melted in a graphite crucible and cast into a steel mold.

Second stage: Sulphide additions to the brass in order to improve the machinability properties without lead addition. Previously cast brass and sulphides are melted and mixed together in graphite crucible and cast into steel mold to obtain lead free brass alloys with comparable machinability.

The first stage includes in the main alloying elements that produce the brass alloy. The second stage includes additions to improve the properties of this alloy. Lead free brass alloys were categorized in two groups for second stage. Brass alloys produced including MnS additives are termed as Group 1, while the ones contain MoS₂ additive are termed as Group 2. Table 2.2 shows the main alloying elements and selected additives to use for charging.

Table 2.2 Alloying elements and additives for charging

		Additives for Alloying Element (Gram)				
	Samples	Cu	Zn	Inter-Mn	S	Al
Group 1	MnS-3	118.55	57.81	14.15	1.06	0.34
	MnS-4	117.74	56.81	16.12	1.54	0.28
	MnS-5	115.89	56.84	17.14	2.04	0.42
		Cu	Zn	Inter-Si	MoS ₂	Al
Group 2	MoS ₂ -1	110.04	52.24	3.45	1.24	0.36
	MoS ₂ -2	108.87	51.47	5.42	2.14	0.54
	MoS ₂ -3	107.98	52.94	6.67	2.97	0.57

The samples were melted in an induction furnace of low frequency in a graphite crucible. High purity copper in the form of sheet and zinc wire which were supplied from a local

supplier were used as charge main alloy materials. Silicon, molybdenum disulfide, metallic manganese and sulfur were used as additives. The chemical composition of copper sheet and zinc wire was determined by XRF before melting and presented in Table 2.3. Copper sheet was wrapped to roller form for replacement inside graphite crucible. The zinc wire was cut to equal lengths. The additives used in casting process were supplied from Labor-Teknik company. The amount of the main alloying elements and additives was adjusted using precision scale to balance chemical composition of prepared samples. All of the prepared samples had the same casting conditions and were poured into the hot work steel mold. On the other hand, graphite crucibles were individually used for preparing each composition to prevent contamination.

The shell of the mold, which molten brass alloys poured into, was made by hot work steel because it shows heat resistance and durable. The sample after casting was 17 mm in diameter and 250 mm in length with feeding part. To prevent splashing during casting, the ingot mold was preheated up to 120°C for 15 minutes in the oven before pouring the molten brass alloys. One of the most important steps in casting was to set the charging time and to adjust quantity well. Silicon based aerosol compound was sprayed on inner surface of ingot mold to protect and lubricate all parts and sample, thus casted sample can be easily removed from ingot mold. Fig. 2.12 shows the pictures taken during casting processes for the sample preparation. Melting of brass samples was performed using induction furnace at approximately 1100 °C with 7.4 kW power.

Table 2.3 Chemical composition of copper sheet and zinc wire

Elements wt. %	Cu	Zn	Sn	Al	Pb	Fe	Si
Zinc Wire	0.0005	99.995	--	--	0.0029	0.0026	0.0017
Copper Sheet	92.8700	--	6.0200	0,0210	--	--	0.2720

Chemical compositions of brass alloys studied and reference samples (i.e. Free Cutting Brass (FCB) and Eco-Brass) was given in Table 2.3.



Figure 2.12 Images captured while producing samples during the casting process

2.4 Metallographic Studies

The microstructural examination of samples can provide information about the morphology and distribution of constituent phases in the microstructure. It is also useful in observing the texture and pattern of certain crystal imperfections and defects.

For metallographic examination each sample was cut from the cast brass billet in two directions namely longitudinal and transversal from the cylindrical samples with a 15 mm diameter and 120 mm height. Then samples were mounted via cold mounting. This method is like a casting process which consists of two materials. One of them is resin which is in liquid form. The other one is the hardener. Next step is the grinding processes. Silicon carbide paper was used to remove plastically deformed layer which occurs during cutting process. The grinding procedure was commenced from 180 grit to end up with 2500 grit.

Mecatech 334 automatic series of grinding and polishing machine was illustrated in Figure 2.13. It has variable and adjustable rotating speed. Individual force is adjustable via pneumatical control system. It is available to grinding or polishing six specimens at once.



Figure 2.13 Mecatech 334 Automatic Grinding Machine using for metallographic studies

In order to reveal microstructure for better examination of each brass sample, electrolytic polishing was performed at 2 volts for 20 sec. with an aqueous solution containing 40% phosphoric acid. As shown in Figure 2.14a, the Olympus BX51M optical microscope was used to examine the microstructural properties of the samples at 50x, 100x and 200x magnifications. Glass desiccator is used to prevent moisture for highly sensible alloying additives and to keep them dry which was shown in Fig. 2.14.b, Fig. 2.14.c illustrates cold mounted samples.



a)



b)



c)

Figure 2.14 Equipment used in metallographic study (a) Optical microscopy (b) Glass desiccator (c) Cold mounted samples

2.5 Corrosion Studies

To examine the corrosion behavior of brass alloys, they are often subjected to two different tests. One of them is dezincification test and the other is stress corrosion crack test. Because brass alloys are susceptible to dezincification as well as stress corrosion crack test.

2.5.1 Dezincification Test

Copper and zinc constituting to brass alloys are one of them due to their different emf series. Dezincification is a corrosive process in which selective leaching takes place in drinking water and removal of zinc occurs from brass, leaving copper rich porous structure. Besides, it is known as special de-alloying in terms of scientific aspect. This corrosive environment results in a decrease in mechanical strength of brass alloys. The failure of brass alloys because of the dezincification is a well-known corrosion examples and very commonly observed in plumbing product industry.

Electrochemical corrosion studies were performed according to ISO 6509 standard using a potentiostat in aqueous solution containing 1 wt. % CuCl_2 solution which was prepared in a 100 ml glass beaker. Corrosion system consists of conventional three electrode system, a saturated calomel electrode (SCE) as a reference electrode, graphite rod as a counter electrode and sample as a working electrode was employed.

The sample with the mounted part was immersed in aqueous solution while the sample with the unmounted part which is outside of aqueous solution was connected to potentiostat device for data acquisition. The open circuit potential (OPC) levels of the samples were measured for 10 minutes after the samples were immersed in the aqueous solution and then OCP values were stabilized. The potentiodynamic potential was scanned for open circuit potential levels from under -0.4 V to over $+0.4\text{ mV}$ with scan rate of 1 mV/s . All experiments were performed at room temperature. The standard electrochemical cell which used for experimental study is shown in Figure 2.15.



Figure 2.15 Standard electrochemical cell used for determination of corrosion rate

2.5.2 Stress Corrosion Cracking

Stress corrosion cracking (SCC) is a special form for corrosion which occurs with the help of harsh environmental condition because of internal stresses. Environment with ammonium trigger to risk SCC due to increasing high internal stress. Brass pipe continuously gets in touch aqueous solution containing ammonia, chlorine, calcium, nitrides etc. Residual stress taken place by non-uniform flows or mechanical working leads to susceptible SCC with time. The test was performed according to ASTM standard B858. All samples were exposed to prepared solution with 1M NH_3 for 24 hours at room temperature.

2.6 Machinability Test

Machinability tests were performed in the Machining Laboratory of the Technology Faculty at Marmara University. Machining operations was performed using a commercial CNC lathe which has 2kW spindle power and highest spindle speed of machine was 2500 rpm. Cutting was conducted using CNMG 1 12-04-08-SF a CVD coated carbide cutting tool. Geometry of cutting tool, cutting speed, feed rate and depth of cut is presented in Table 2.4

Table 2.4 Cutting Tools Type and Machining Operation Conditions.

Geometrical features of cutting tool:	Cutting velocity	Feed rate	Depth of cut
-6° rake angle. 7° clearance angle. Nose radius: 0.8mm	(Vc) 50m/min 1500Rpm*(D=15mm)	(f) 0.2 mm/rev	(doc) 1.0 mm

Machinability test has four main criteria which are cutting force, surface roughness, chip formation, cutting tool wear [22,23]. Cutting tool wear requires an exceptionally long process in the machinability of brass materials and relies on cutting force. Therefore, two main criteria were chosen to determine machinability of brass which are chip formation and surface quality.

2.7 Surface Roughness Measurements

The measurement of surface roughness for samples was carried out using Mitutoyo SJ-201P instruments depending on arithmetic roughness average from turning surface which was shown in Figure 2.16. Surface roughness measurements were performed at four different points on cylindrical sample surface along with one-centimeter length.



Figure 2.16 Surface Roughness Testers MITUTOYO SJ-201P

2.8 Mechanical Test

2.8.1 Tensile Tests

The brass samples prepared by casting method were machined by using CNC lathe to form tensile test samples in accordance with EN-ISO 6892. Measurement of tensile strength of 3 samples produced by casting under the same conditions and from the same composition were carried out using Deviatrans universal testing machine with 5mm/min strain rate. The tensile test equipment and tested samples are shown in Figure 2.17.



Figure 2.17 The images of tensile testing instrument and tested samples

2.8.2 Hardness Test

Hardness test of both longitudinal and transverse cross-section of casting samples were performed using HMV- 2T. Shimadzu microhardness tester was employed under 200 gf for 15 seconds at room temperature. The value of hardness measurement is in micro Vickers scale. Measurements were conducted on 5 different regions of the sample starting from side of sample to the center of the sample. Hardness tester was illustrated in Fig.2.18.



Figure 2.18 HMV-2T Shimadzu brand hardness tester used for determination of microhardness.

2.9 Wear Test

Cylindrical wear test specimens were cut to the range of about 15 mm and 20 mm distance to put socket of circular disc sample connected to wear device. The surfaces of the samples were firstly visually checked if they are flat or not for wear testing. Before wear test was performed, the weight of each sample was measured with precision balance scale with accuracy of ± 0.001 mg. Wear test was carried out via pin-on-disk tribometer at room temperature in a dry condition. Wear pin ring has spherical shape with 3mm radius and produced by using AISI 52100 steel. The pin is stationary, and the disk can be rotated itself with 360° angle. Pin-on disk tribometer device and its equipment was shown in Fig. 2.19. The value of friction coefficient has calculated and displayed instantly through employed computer screen which is connected to pin-on disk tribometer device. Test parameters were employed shown in Table 2.6 depending on the previous experimental studies and pre-wear test results. Weight of samples measured before and after the test to find out percentage of weight loss.



Figure 2.19 Pin-on Disk Tribometer Device used for determination of wear rate

Table 2.5 Wear Test Parameters

Wear Test Parameters	
Sliding Speed	0.1 m/s
Sliding Distance	50 m
Constant Normal Load	10 N

3 RESULTS AND DISCUSSION

3.1 XRF Spectrometer Analysis

After the machinability test, XRF device has been used to determine the chemical composition of samples and the chemical analysis results of the samples are shown in Table 3.1.

Table 3.1 Chemical compositions of Brass alloys investigated in this study a) MnS including brass, b) MoS₂ including brass and c) Reference samples

		Elements (vol. %)										
	Samples	Cu	Zn	Sn	S	Mo	Al *	Pb	Mn	Fe	Si	Ni
a	MoS ₂ -1	64.33 (±0.88)	31.53 (±0.68)	3.46 (±0.02)	0.155 (±0.14)	0.212 (±0.08)	-	-	-	-	0.341 (±0.06)	-
	MoS ₂ -2	63.45 (±0.61)	31.53 (±0.53)	3.62 (±0.01)	0.25 (±0.52)	0.345 (±0.03)	-	-	-	-	0.924 (±0.22)	-
	MoS ₂ -3	64.55 (±0.79)	30.83 (±0.41)	2.73 (±0.01)	0.628 (±1.14)	0.421 (±0.29)	-	-	0.107 (±0.01)	-	1.612 (±0.38)	-
b	MnS-3	63.31 (±0.49)	31.29 (±0.22)	3.6 (±0.04)	0.342 (±0.79)	-	-	-	1.38 (±0.07)	-	-	-
	MnS-4	63.95 (±1.06)	29.9 (±0.79)	3.88 (±0.03)	0.194 (±0.21)	-	-	-	1.92 (±1.13)	-	-	-
	MnS-5	64.18 (±1.12)	29.42 (±0.97)	3.78 (±0.12)	0.181 (±0.06)	-	-	-	2.33 (±0.31)	-	-	-
c	FCB (lead added)	57.38 (±0.67)	38.98 (±0.11)	0.292 (±0.02)	-	-	-	2.9 (±0.01)	-	0.297 (±1.05)	-	0.118 (±0.83)
	Eco-Brass (Si added)	75.14 (±0.75)	21.81 (±0.25)	0.047 (±1.02)	-	-	-	0.093 (±0.09)	-	0.063 (±0.00)	2.81 (±0.83)	-

*Al is not detected in the chemical analysis, but Al is added during the mixing of the batch before melting to prevent Zn oxidation preferentially.

The elemental data are based on volumetric fraction within certain determined by the factor called the 2-sigma error. For example, if this value is 95% certain that the actual value varies no more than this amount from the reported value. Longer analysis duration resulted in a decrease on the 2-sigma error, however even in long analysis durations; complete elimination is not possible. Detecting light elements requires long analysis durations as these elements are prone to create auger electrons rather than characteristic X-Rays. Furthermore, the amount of sulfur in the alloys might be below detecting limit of the spectrometer used in this study. Therefore, volumetric percentage of elemental sulfur in alloys vary widely.

3.2 X-Ray Diffraction Analysis

X-ray diffraction analysis was carried out on all cast samples and reference samples to evaluate phase composition. The analysis of XRD patterns, which are compatible with standard ICDD PDF cards, was performed by X'Pert Highscore plus software. The result of XRD analysis for samples prepared with MoS₂, MnS additives and reference samples are presented in Figure 3.1 and Figure 3.2, respectively. From the result of XRD Analysis on samples prepared with MoS₂ additives, the peaks at 42.36°, 49.64° and 72.24° were detected on diffraction pattern which correspond to alpha phase. In addition, the peaks appeared at 43.28°, 62.87° and 79.39° are beta prime phase. The peak at the diffraction angle of 42.36° belongs alpha phase with a (1 1 1) crystal plane and the peak at the diffraction angle of 43.28 ° also belongs to beta prime phase with a (110) crystal plane. These peaks have a high intensity on diffraction pattern for each sample. The minor three peaks on F.C.B brass appeared at 31.37°, 36.34° and 62.30 ° which are regarded to be peaks of element lead. On the other hand, the diffraction pattern of Ecobrass is distinct from the other samples, with additional peaks at 39.97° and 45.59°, apart from peaks of alpha phase, which are considered to be main peak of Cu₄ZnSi phase. The presence of this phase has been reported in previous studies [86]. When XRD analysis results of samples prepared with MoS₂ additives were examined, it was observed that the alpha phase peak intensities were higher than the beta phase peak intensities for MoS₂-1 sample. Peak intensity of beta phase for samples prepared with MoS₂-2 and MoS₂-3 additives which was more intense than peak intensity of beta phase for sample prepared with MoS₂-1. This case indicated that the increase of the silicon content in microstructure promotes the beta prime phase formation. This result is in agreement with the results of SEM-EDS

analysis (see Figure 3-8) and is supported by the other studies.[52], [54], [87]. When the results of XRD analysis of the samples prepared by MnS additives are examined, the peak intensities of alpha phase were higher than the peak intensities of beta prime phase for samples prepared by MnS addition except MnS-5 sample on the diffraction pattern. The peak at 42.36° which belongs alpha phase with a (111) crystal planes for MnS-3 sample is more intense than the peaks of other samples due to having much more grains which grows into (111) crystal planes during solidification.

Furthermore, volume fraction of beta prime phase and alpha phase were calculated by using the equation given below where V_{α} is volume fraction of alpha phase [88].

$$V_{\alpha} = \frac{(\text{Total values of alpha phase intensities})}{\text{Total values of alpha phase intensities} + \text{Total values of beta prime phase peak intensity}} \quad \text{Eq. 3.1}$$

Using the same equation, the volume fraction of the beta phase is calculated. Volume fraction of beta prime phase and alpha phase for all prepared samples are presented in Table 3.2. to compare MnS and MoS₂ added samples. The increase of the volume fraction of the beta prime phase in the microstructures of MoS₂ samples can be attributed to the increase in the amount of silicon. Moreover, it is thought to increase the beta prime phase with Mn increase in microstructure of MnS samples. Most of the additives except nickel additive promote the ratio of beta phase formation [89]. Detailed information will be given in Section 3.8.

Table 3.2 Volume fraction of alpha and beta prime phases for all prepared samples.

Sample Codes	Alpha Phase (vol. %)	Beta Prime Phase (vol. %)
MnS-3	0.842349	0.157651
MnS-4	0.755426	0.244574
MnS-5	0.578668	0.421332
MoS ₂ -1	0.808646	0.191354
MoS ₂ -2	0.305895	0.694105
MoS ₂ -3	0.182758	0.817242

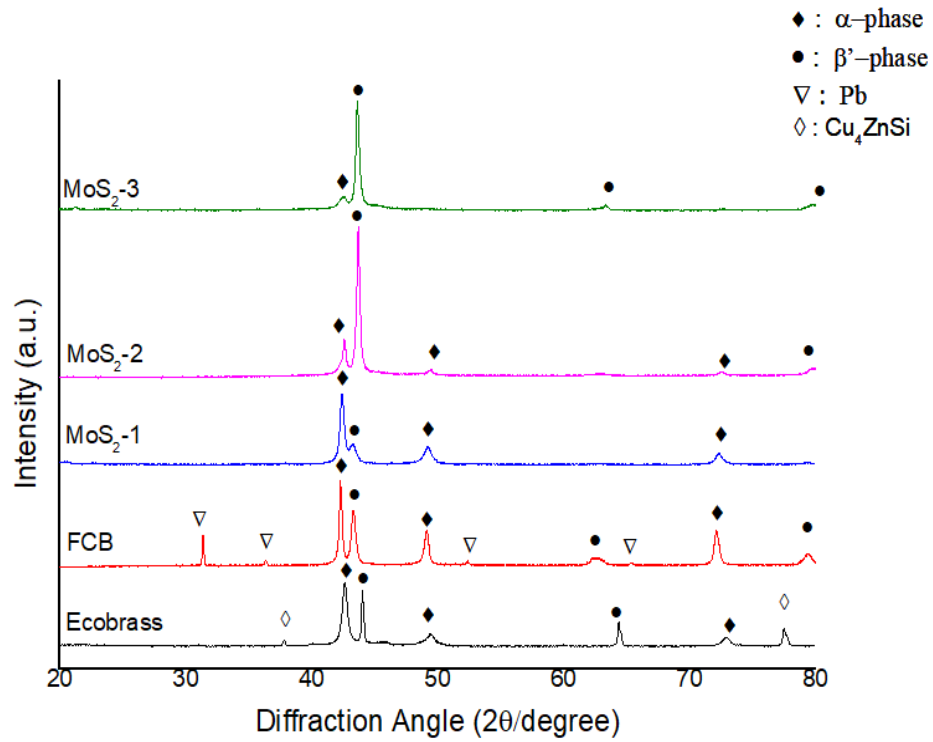


Figure 3.1 XRD patterns of brass having various amount of MoS_2 added into brass

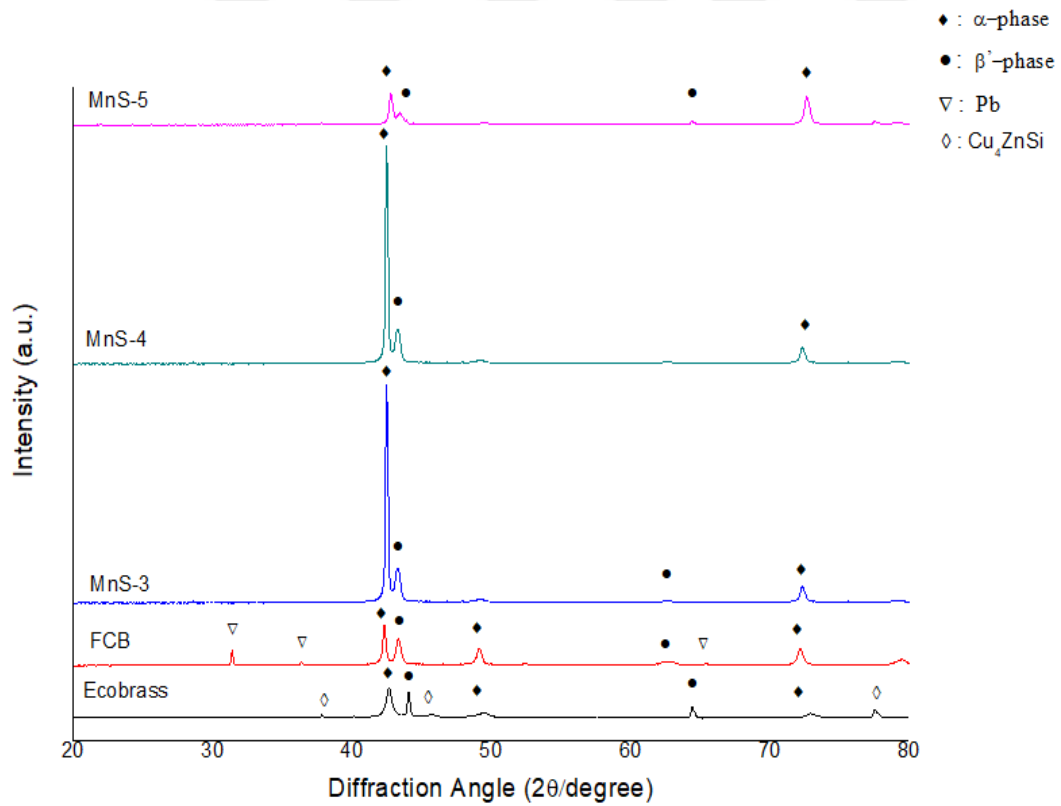


Figure 3.2 XRD patterns of brass having various amount of MnS added into brass

Figure 3.3 shows XRD analysis graph given above, which is scanned in a narrow angle. It can be seen that 2θ angle value of Ecobrass shifted to a higher angle due to micro-strain which occurs because of the presence of silicon element in Ecobrass microstructure. Because silicon acts as a substitutional atom which replaces zinc atom, therefore lattice-induced tensile stress occurs in unit cell by virtue of difference in atomic radius between silicon (1.11 Å) and zinc (1.34 Å) [90]. The reason of the peak being broader for Ecobrass sample might be due to the formation of sub-grains and micro-strain.

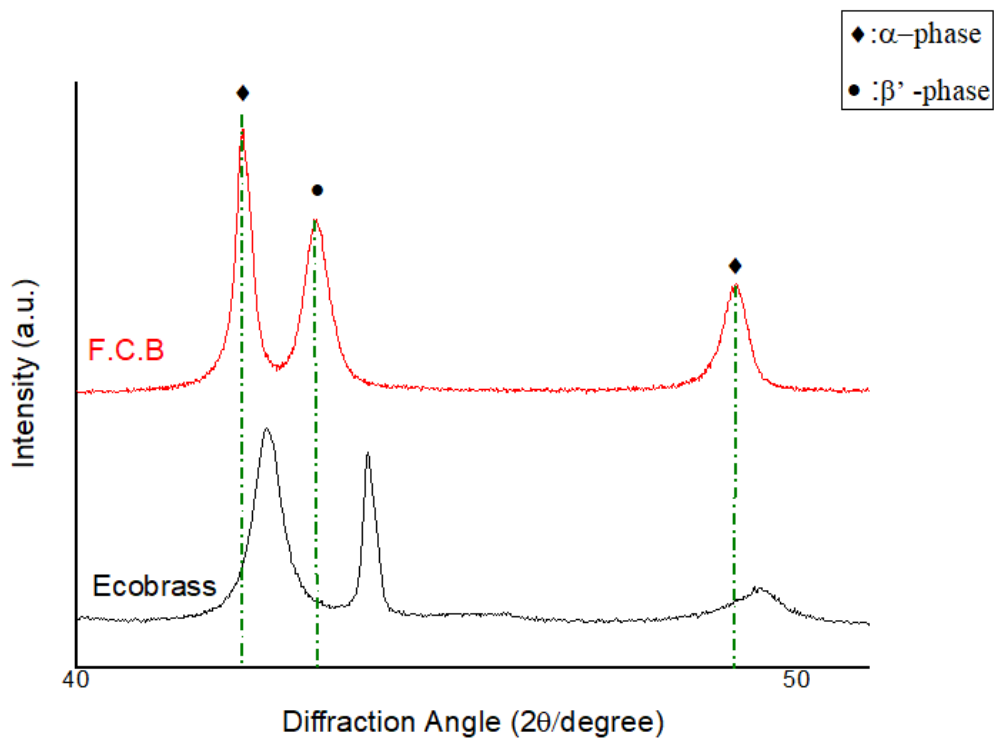


Figure 3.3 XRD patterns comparison of samples F.C.B and ECOBRASS with narrow scan.

Table 3.3 presents the phases detected in samples of XRD analysis. From XRD analysis results, all the samples generally consist of alpha and beta prime phase. Apart from these phases, in reference samples element lead was detected for F.C.B and Cu_4ZnSi phase for Ecobrass. According to working principles XRD does not detect phase which have α volume fraction lower than 3 vol. %. As it can be understood from this result, if the volumetric fraction of intermetallic compounds in the microstructures is below 3 vol. %, it should be identified with another characterization method.

Table 3.3 Comparison of phases detected by XRD analysis

Sample Codes	Phases detected	JCPDS numbers
FCB	$\alpha - \beta'$ - Pb	50-1333 (α), 65-2873 (Pb), 65-6566 (β')
Eco Brass	$\alpha - \beta'$ - Cu ₄ ZnSi	50-1333 (α), 65-6566 (β'), 35-1152 (Cu ₄ ZnSi)
MnS -3	$\alpha - \beta'$	50-1333 (α), 65-6566 (β')
MnS -4	$\alpha - \beta'$	50-1333 (α), 65-6566 (β')
MnS -5	$\alpha - \beta'$	50-1333 (α), 65-6566 (β')
MoS ₂ -1	$\alpha - \beta'$	50-1333 (α), 65-6566 (β')
MoS ₂ -2	$\alpha - \beta'$	50-1333 (α), 65-6566 (β')
MoS ₂ -3	$\alpha - \beta'$	50-1333 (α), 65-6566 (β')

3.2 Microstructure Examination by Optical Microscopy

Figure 3.4 and Figure 3.5 show the optical micrographs of Free Cutting Brass (FCB), Eco Brass and samples prepared with MnS and MoS₂ additives respectively in optical micrograph. All optical microscope images belong to longitudinal section of the as-cast brass samples except commercial FCB and Eco Brass. The samples of FCB and Eco Brass were investigated metallographically on cross section. It is known that chemical composition and microstructure have a great influence on the mechanical properties and machinability of brass alloys. All samples having chemical composition range of 38-43 wt. % zinc content consists of dual phase (alpha and beta prime) and the presence of these phases also have been proved by X-ray diffraction analysis data (see in Figure 3.1, 3.2). FCB and Eco Brass have a similar microstructure exhibiting columnar and equiaxed grains with average size of about $\sim 5\mu\text{m}$ for Eco Brass and about $\sim 30\mu\text{m}$ for Free Cutting Brass (F.C.B). On the other hand, cast copper microstructure is formed by non-uniform grains with very different sizes. According to metallographic studies, commercial free cutting brass and Eco Brass samples have polyhedral microstructure. These microstructures reveals that brass samples were produced by means of extrusion processes [91]. Ecobrass has a smaller grain size than Free Cutting Brass due to the presence of silicon. Silicon is known both to act as grain refiners and suppress to alpha grains' growth in dual phase brass alloys [82,83]. Black spots are dispersed lead in the microstructure of F.C.B. In the previous study, it was reported that the black dots or stripes seen on the optical microscope image of the F.C.B represent lead particles.

Each of the reference samples has alpha-beta duplex phases. In micrograph, alpha phase appears in light and beta prime phase appears in darker. The alpha phase which has high solubility of zinc in copper matrix, which forms solid solution with FCC crystal structure. The beta prime phase is ordered intermetallic phase with stoichiometry of Cu-Zn and has BCC crystal structure to be formed from disordered beta phase at temperature of below 460 °C [94]. It can be seen in micrograph of FCB (see in Fig. 3. 4. a) that lead is insoluble in both alpha and beta prime phases and appear as isolated black dots. Lead phase is small and numerous in the grains while segregation has occurred in a pelletized form located at grain boundaries. From the results of XRD analyses (see in Fig 3.1) alpha-beta duplex phases were identified in the microstructure of samples. The distribution and appearance of these phases were affected by their process method and solidification rate.

Samples prepared with addition of various amounts of MnS have a distinct microstructure that gives contrast due to different reflectivity of diversely oriented dendrites. Dendritic structure is typically found in as- cast microstructure of copper alloys. First solidified metal is pure copper, then followed by zinc to turn into copper and zinc alloy that leads to coring dendritic structure. A composition gradient emerges between dendrite core and outer edge, zinc content at the center of dendrite is nearly zero and zinc content increases from core to the outer region of dendrite. Alloys having a broad solidifying temperature range reveal such a composition gradient which is called coring in the microstructure [93]. The microstructure of MnS-3 sample exhibits α - Widmanstättén structure because of having moderate cooling rates, alpha phase that gives contrast precipitates with both plate and needle-like formation in beta prime matrix (dark contrast) to minimize strain energy in microstructure. Liquid metal alloy turns into beta phase as a result of hyper-peritectic reaction at the beginning of solidification ($L + \alpha \rightarrow \beta$). The α - Widmanstättén precipitation nucleates and distributes in all of the beta matrix as temperature decreases [62]. Lastly, solidification is completed with transformation from disordered beta to ordered beta prime phase. The formation mechanisms of Widmanstättén structures for Cu-Zn-Si ternary alloys have been emphasized by the previous study [92]. The microstructure of MnS-4 has become a partly dendritic structure from Widmanstättén structure by increasing undercooling rate. The distance between the dendritic arms change due to the cooling rate. The larger the dendritic arms, the slower the undercooling rate. The microstructure of MnS- 5 is completely formed with dendritic structure.

The microstructure of the samples prepared by adding various amounts of MoS₂ is presented in Figure 3.5. The microstructure with the small needle-like formation of Widmanstätten morphology emerges in the micrograph of the MoS₂-1 sample. As silicon content of prepared alloy increased, the Widmanstätten precipitates only appear with small needle-like formation at the beta phase grain boundary region in the microstructure of MoS₂-2 as shown in Figure. 3.5.f

The microstructure of MoS₂-3 consists of beta grains in the matrix due to having high content of silicon than other MoS₂ alloys. This case is consistent with XRF results (See Table 3.1). With increasing silicon content, alpha phase reduces and turns into beta phase which is dominant phase in the microstructure in addition to promote the formation other phases [54]. Not only addition of silicon but also addition of tin into brass increases volume fraction of beta phase in the microstructure [73]. Based on the results, the microstructure of samples with Si content consists of α - β dual phases and also peritectic reaction takes place even at lower zinc content because Si has strong influence on the formation of beta phase [92].

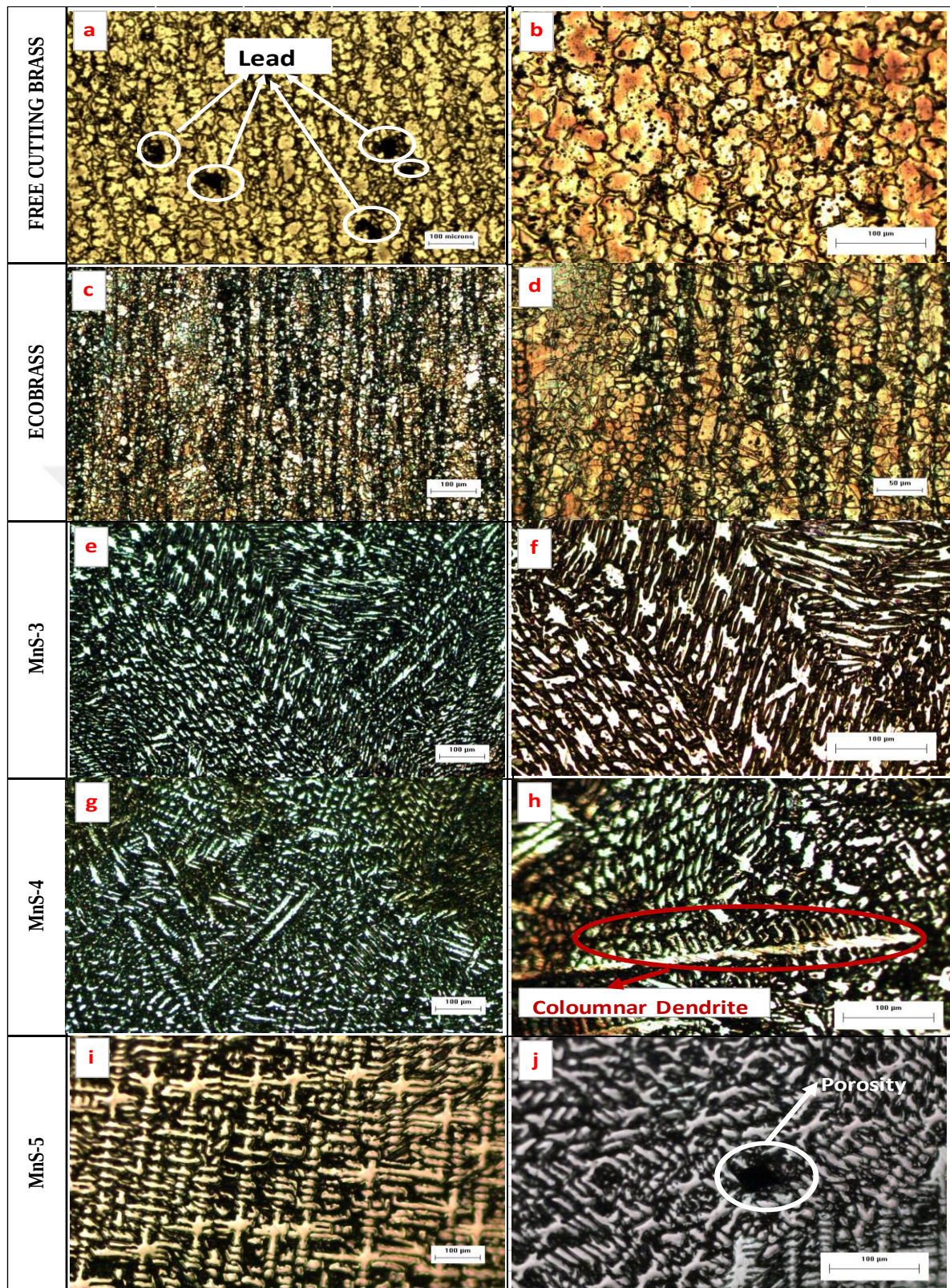


Figure 3.4 Microstructures taken from optical microscope a) x50 b) x100 for F.C.B, c) x50 d) x100 for EcoBrass, e) x50 f) x100 for MnS-3, g) x50 h) x100 for MnS-4, i) x50 j) x100 for MnS-5

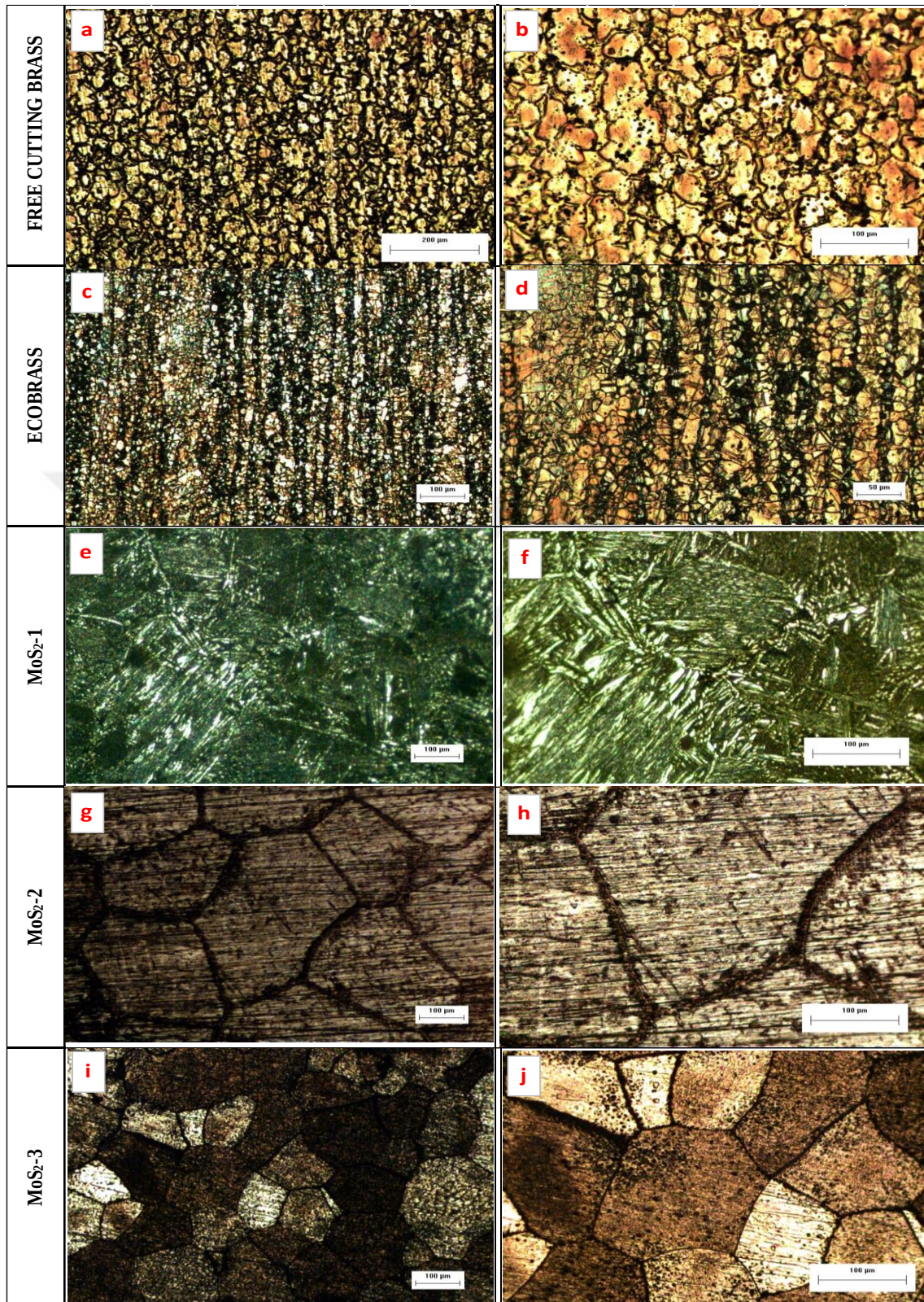


Figure 3.5 Microstructures taken from optical microscope a) x50 b) x100 for F.C.B, c) x50 d) x100 for EcoBrass, e) x50 f)x100 for MoS₂-I, g) x50 h) x100 for MoS₂-II, i) x50 j) x100 for MoS₂-III

3.3 Microstructure Analysis and Examination by Scanning Electron Microscopy

The longitudinal cross-sectional SEM images of prepared and reference samples were shown in Figure 3.6. The SEM image on FCB microstructure revealed typical α - β dual phase structure. Lead particles reveal as white phase with a distinct contrast image and are homogenously distributed at grain boundaries in brass matrix. During solidification, the lead particles which maintain liquid form due to lower melting point which provides good coalescence at the grain boundaries. The microstructure of Eco Brass consists of large and small grains and, intermetallic compounds which is precipitated at grain boundaries. This observation is in very good agreement with the microstructure of other study [95] of which intermetallic compounds precipitated at the grain boundaries. Several of the grains formed with annealing twins due to the fact that they were subjected to extrusion and annealing treatment and also dominant phase in the microstructure is beta prime phase although lead island and IMC's phase is present with a minor distribution. Sem images of MnS-3 and MoS₂-1 samples having Widmanst etten structure reflects a typical cast structure. Two types of Widmanst etten structure are observed, one of them is needle-like shape which appears in MoS₂-3 and the other formed with both needle and plate shape. The island structure shown in Fig. 3.6.d has different view of Widmanst etten structure in terms of appearance and has the same morphology with Widmanst etten structure. One study emphasized that the island structure is a parallel view of the needle structure [96]. This case resembles different views such as front, top and side views in technical drawing.

Solidification of the alloys having Widmanst etten structure begins with a hyper-peritectic composition. During solidification, beta phase occurs after peritectic reaction between liquid and the prime alpha phase and, the brass matrix entirely comprises of beta phase because prime alpha completely dissolves. As the temperature decreases, alpha crystals precipitate below α - β solvus line with random orientation at grain boundaries in beta matrix. The ordering transformation takes place as temperature reaches at about 450° C, beta phase (disordered) is transferred to beta prime phase (ordered), so the zinc atoms are regularly aligned in BCC unit cell [82-83]. The nucleation and growth rate among grains determines plate and needle like formation due to mobility of atoms. Low and moderate cooling rate leads to faster mobility and thus increases the probability of plate formation; on the other hand, rapid cooling rate leads to low mobility, and needle structure

forms in the matrix [99]. The other parameter is alloying elements which influences mobility of atoms. Alloying elements having larger atomic radius have low mobility and hinders immigration of atoms in unit cell because of local strain.

SEM image of MnS-4 is a typical dendritic microstructure. (Fig. 3.6. e) There are two different type regions in which the hollow region and the bunched region that are symbolized as alpha and beta prime phases, respectively. On the contrary, a change in the distribution of α - β dual phase is observed in SEM micrograph of MnS-5 in Fig. 3.6. g. It was observed that the alpha phase precipitated at the grain boundaries of beta phase like intermetallic compounds. The microstructure of MoS₂-2 with increasing silicon contents consist of large beta grains and the Widmanstätten α which nucleates and grows with acicular morphology inside grains and at the grain boundaries. SEM image of the MoS₂-3, which was taken from the entire surface, was shown in Figure 3.6. It shows large beta grains and intermetallic phase regions that precipitated at grain boundaries.

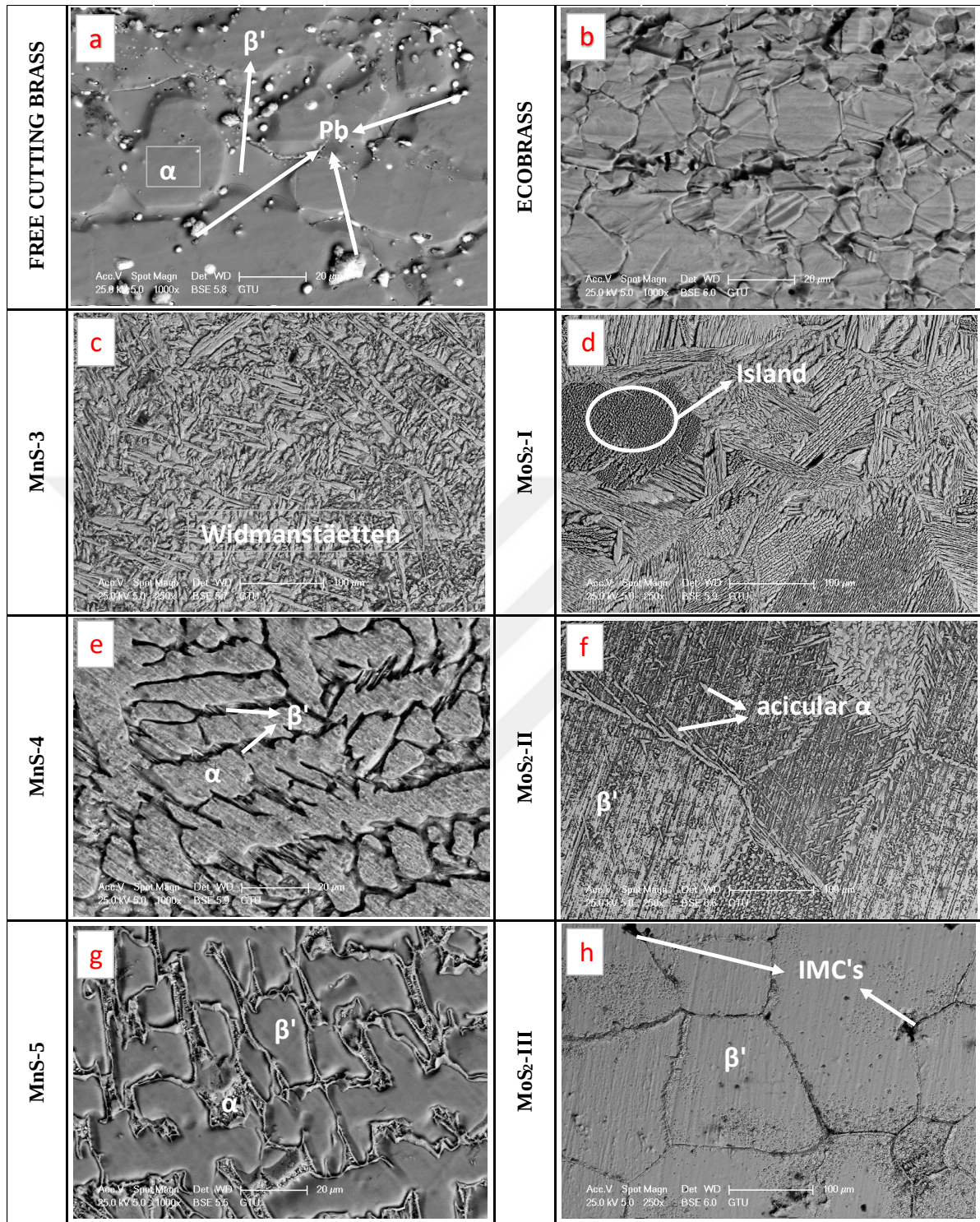
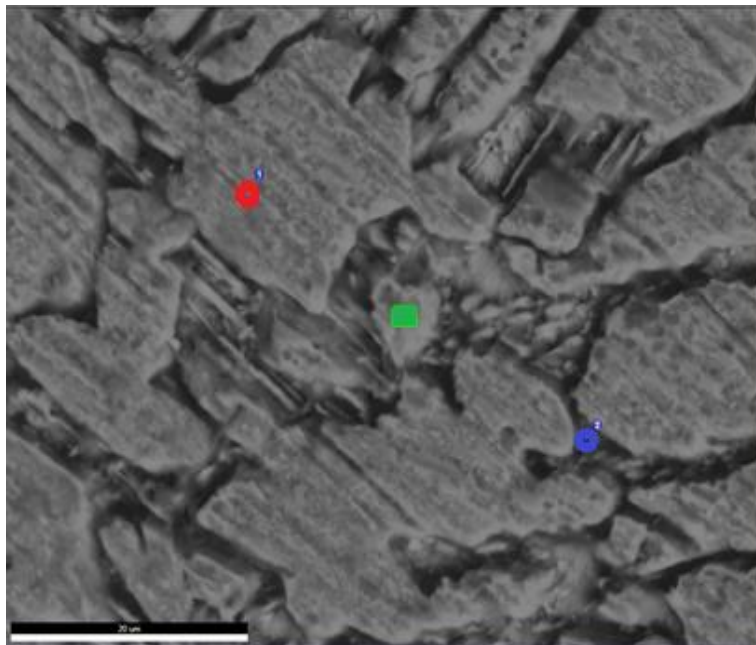


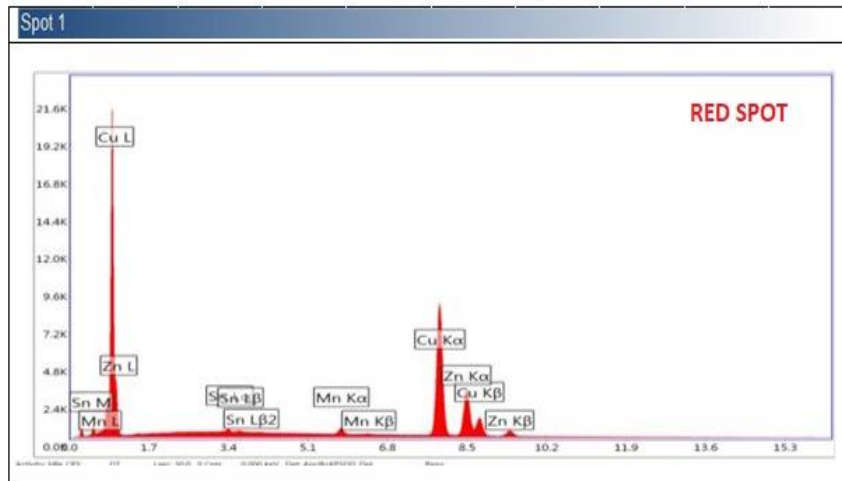
Figure 3.6 Comparison of SEM Microstructures of all samples a) F.C.B, b) EcoBrass ,c) MnS-3, d) MoS₂-I, e)MnS-4, f) MoS₂-II, g)MnS-5, h) MoS₂-III

Point and area quantitative chemical analysis using EDS equipment, which is attached to SEM, is carried out to identify fraction of each element in the microstructures of MnS-4 and MoS₂-3 samples and is shown in Figure 3.7 and Figure 3.8, respectively. Alpha, beta

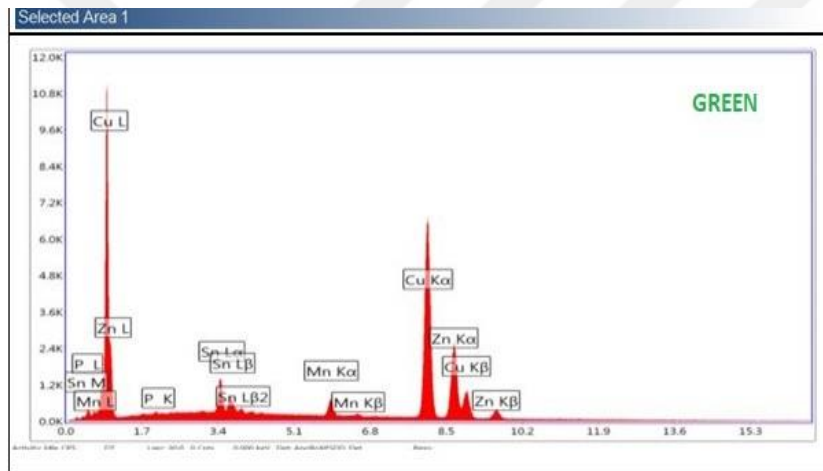
phase regions and Sn-Mn rich intermetallic phase at alpha-beta interface (in Figure 3.7.c) were determined by analysis of three different points in SEM-EDS on MnS-4 microstructure. Since the alpha-beta phase interfaces are not thermodynamically stable regions, secondary phases preferentially precipitated to lower their interfacial energy in those places. Generally, higher intensity of Zn on SEM-EDS spectrum indicates beta phase but for this sample is not observed due to its low intensity and poor signal of Zn element which is influenced by surrounding matrix material. Small quantity of phosphorous element descended from base metal which was detected in Sn-Mn rich intermetallic phase. The signal of low intensity Si has come out on the spectrum of MoS₂-3. Besides Si precipitation was observed with equiaxed dendrite morphology at grain boundaries in beta matrix as shown in Figure 3.8 (Red rectangular). The existence of phosphorus and an unidentified peak on spectrum for black dots in beta matrix is proved by the result of SEM-EDS analysis. It would not be easy to compare the solubility of the silicon element in both alpha and beta phases from current results. However, it could be said that Si did not form a new solid solution phase with both phases. In addition, silicon element increases the fraction of beta phases [94].



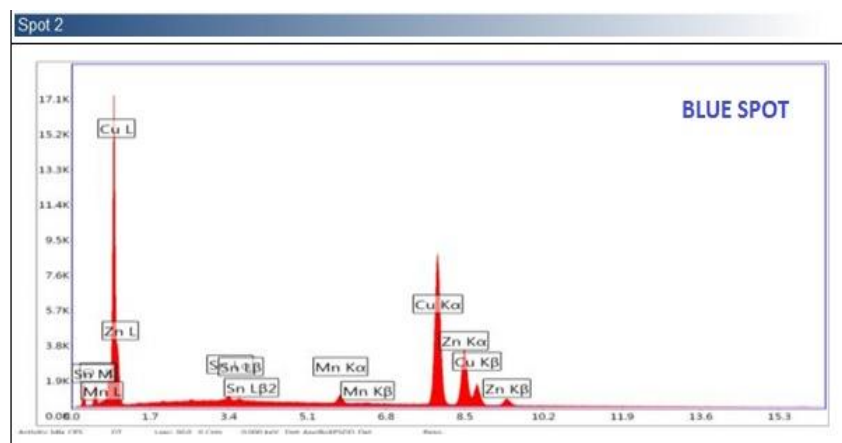
a)



b)



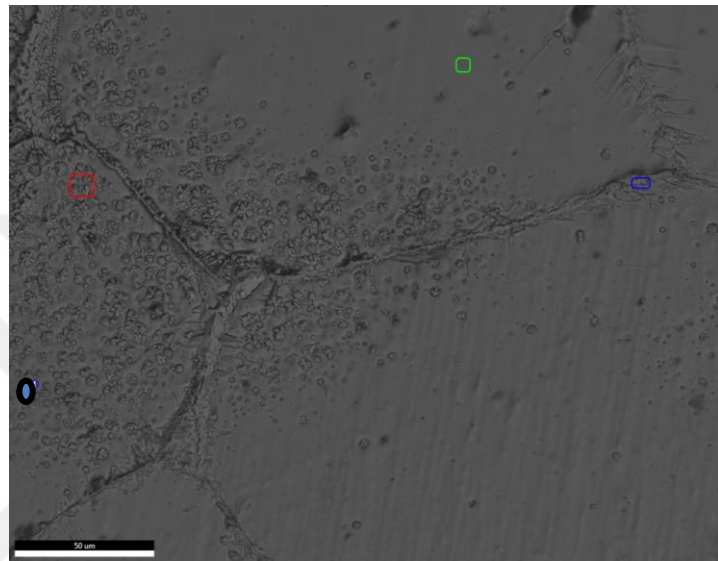
c)



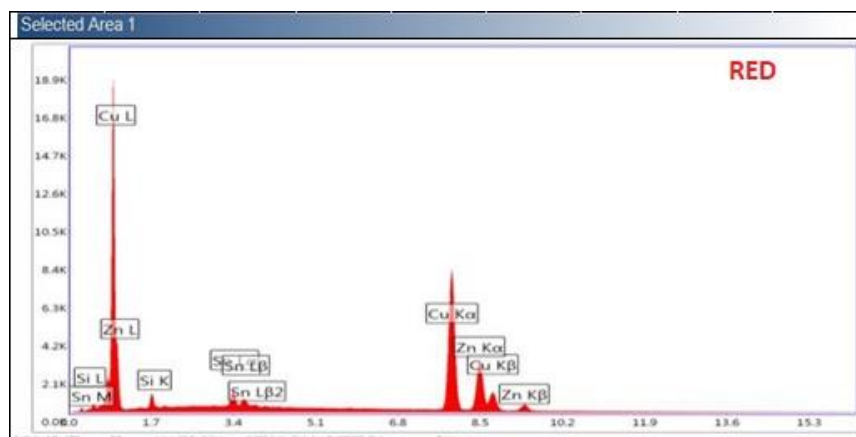
d)

Figure 3.7 The result of EDS analysis from cross-section part of MnS-4 sample a) SEM image
b) red spot c) green area d) blue spot

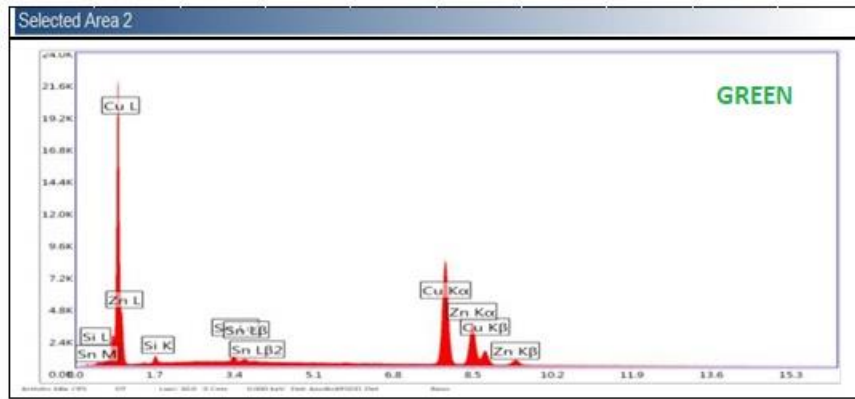
K lines for Cu element give higher peak in some phases, lower in other phases in EDS analysis. The signals of K lines have a greater intensity than the L lines for each material but as the energy of the incident beam value is lower, L lines may be at a greater intensity than the K lines in rare cases. At the same time, particle size and distribution of phases influence the background.



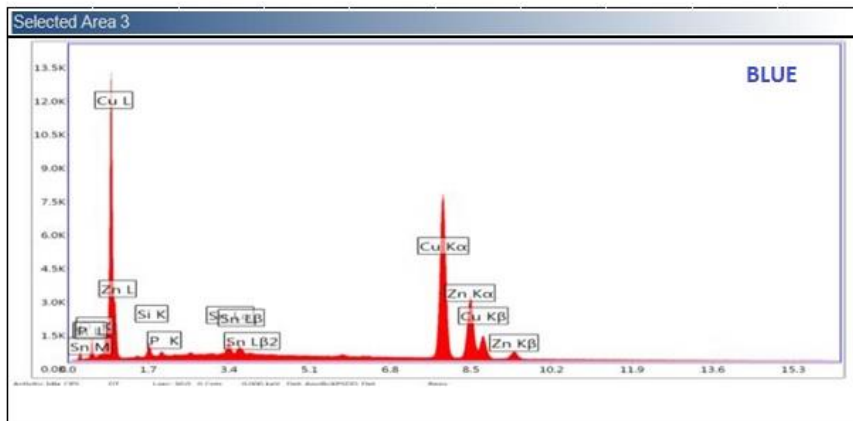
a)



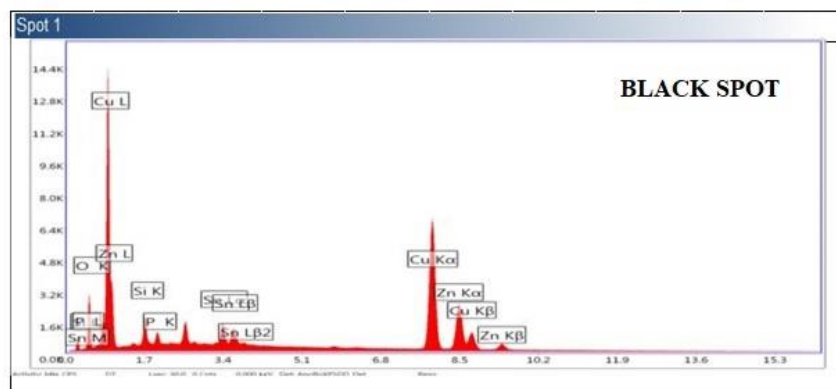
b)



c)



d)



e)

Figure 3.8 The result of EDS analysis from cross-section part of MoS₂-3 sample a) SEM image b) red area c) green area d) blue area e) black spot

Sulphur is hardly detected for MoS₂ containing sample by EDS analysis due of its volatile nature when X-Ray beam is exposed to the selected area. Thus, EDS analysis with scanning map mode was performed by low (5kV) voltage value and the map is shown in Figure 3.9. The result of EDS analysis has exhibited the existence of Cu, Zn, Si and trace amount of sulfur but no signal of Mo element is detected. Silicon precipitation at grain boundaries separated from beta matrix is clearly visible

As emphasized in a previous study MoS₂ reacts with copper to form Cu₂S at a temperature interval between 1000 – 1250°C, and Mo participates into slag [30]. The same study has also suggested that the solid state of MoS₂, which has a high melting point, reacts with copper to form a Cu₂S phase with a metastable peritectic reaction, based on the temperature vs free energy graph (see in Figure 3.9). This case was approved by XRF analysis result which was presented in Table 3.4.

Table 3.4 Chemical Composition of MoS₂-3's slag after casting process

Elements in Slag	Cu	Zn	Sn	W	Mo	Fe	Zr	Nb
wt. %	22.45	41.2	2.04	2.01	28.44	0.109	0.072	0.503

Figure 3.10 shows standard free energies versus temperature for Cu, Sn, Zn, and Mo sulfides form. The values of standard free energy for reaction 1 are positive as increasing temperature; on the other hand, the values of standard free energy for reaction 2 goes to the negative from the point of 780 K temperature. As the standard free energy of the reactions is the most negative therefore it is thermodynamically possible to occur. For this reason, the reaction between MoS₂ and Cu could end up the formation of Cu₂S. Apart from Cu sulfide forms, Zn and Sn which are an alloying element for brass alloys that need to be studied whether MoS₂ is stable or not in these conditions. Figure 3.19.b shows the standard free energies ranging from 273 to 1600 K temperature. The standard free energies for the reactions of 4 and 3 is positive and negative in the order given at between 1000 K and 1100 K temperature performed the casting process. This recommends that reaction 4 between MoS₂ and Zn is accomplished, carried out the formation of ZnS from the view of thermodynamic laws. However, reaction kinetics also come into play in addition to thermodynamics and can determine the transformation rate as well. Most

common example is cementite (Fe_3C), which is a metastable phase, but the transformation rate is so slow so that the transformation into graphite does not occur.

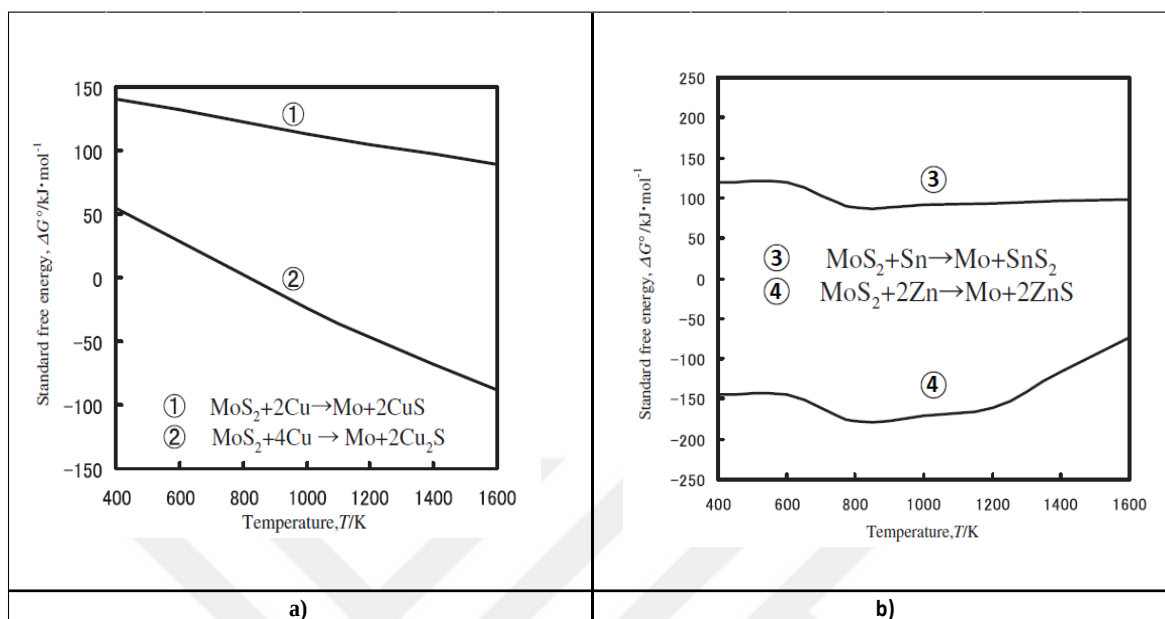


Figure 3.9 Standard free energies a) for Cu sulfides b) for the reaction of Sn, Zn and with MoS_2 [30]

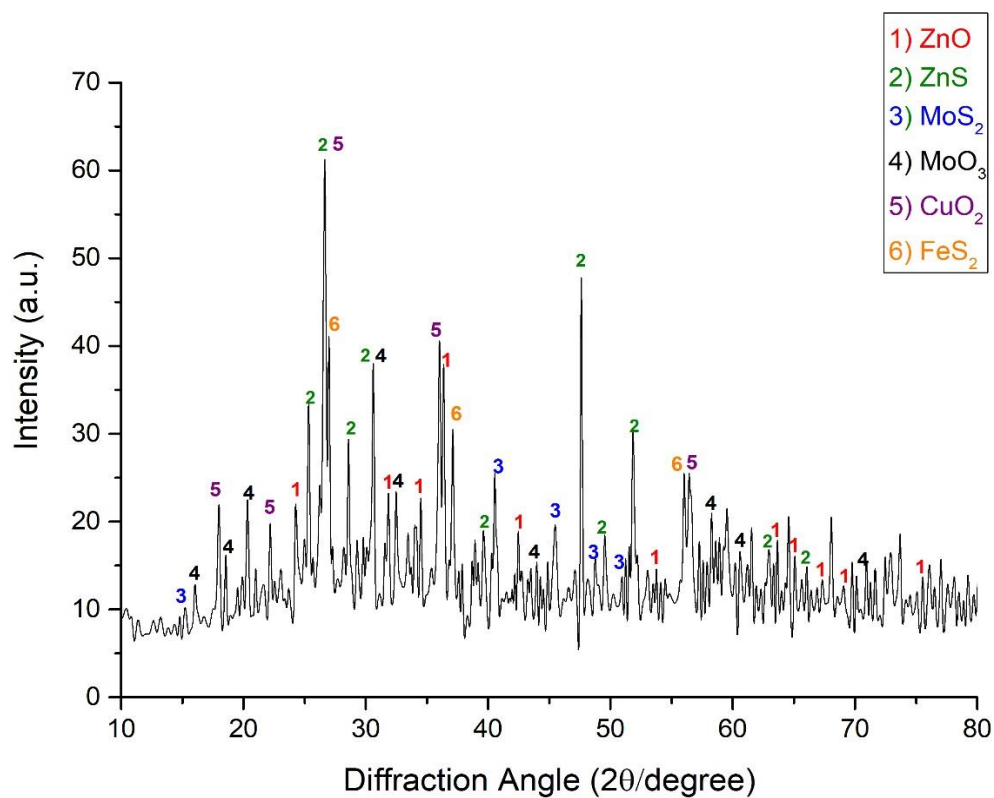


Figure 3.10 XRD pattern for slag of MoS_2 -2 sample

Figure 3.11 shows the XRD pattern of the MoS₂-2 sample's slag phase analysis. As a result of the analysis, sulfur and oxide compounds of Zn, Mo and Cu elements were determined. Apart from this, the presence of iron sulfur in the slag was also detected. Probably this can be attributed to the reaction of iron caused by contamination of the crucible with sulfur at high temperature. Another important issue is the existence of MoS₂ in slag analysis. This means that MoS₂ had partially reacted with brass and some other unreacted part or excess part was directly joined into the slag as oxide and sulphide form.

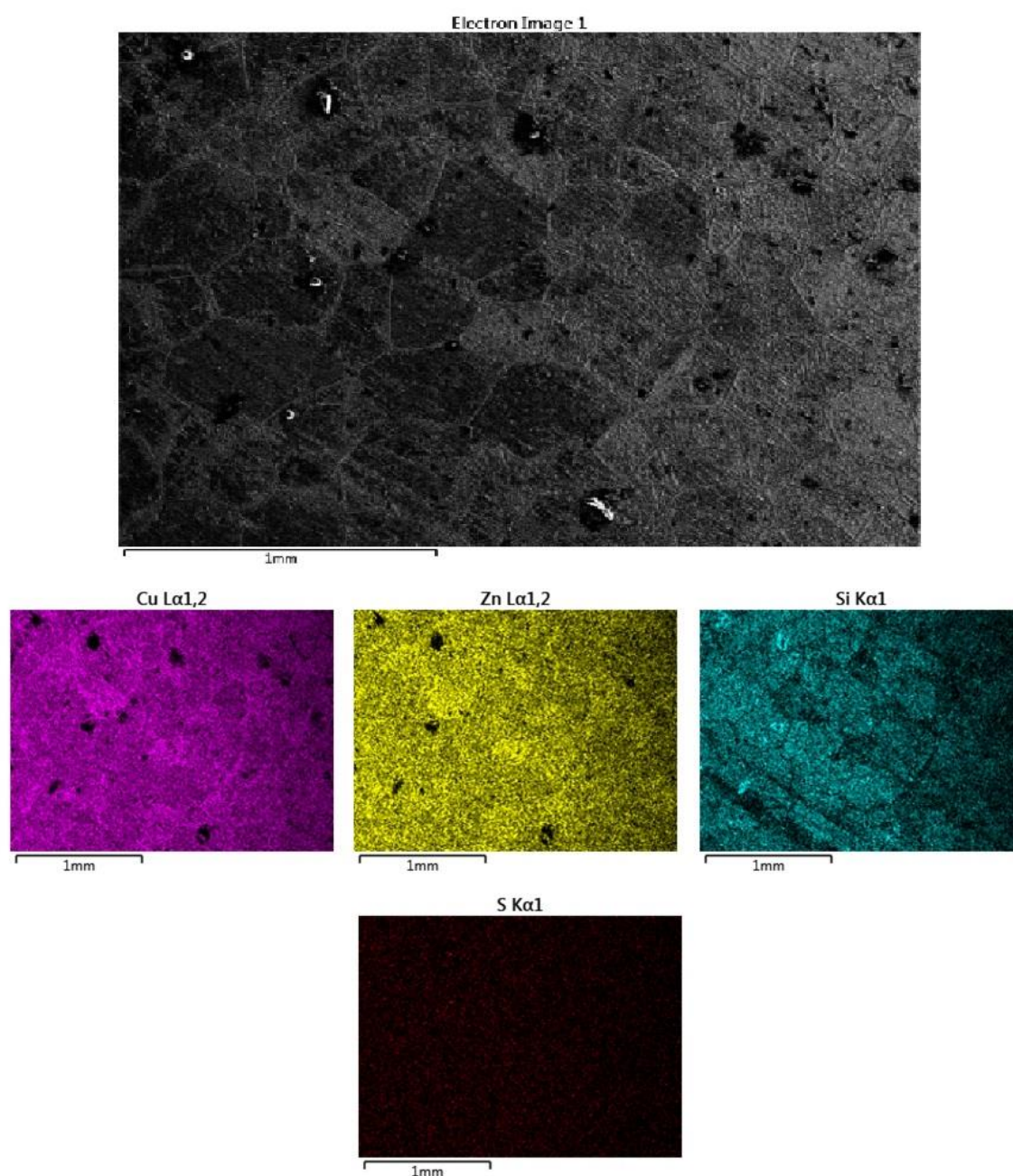


Figure 3.11 Secondary electron image and SEM-EDS maps of MoS₂-3 sample

3.4 Mechanical Tests

3.4.1 Hardness Test

The column bar graph for average hardness value of all samples is shown in Figure 3.12. One of the reference samples is EcoBrass which has highest hardness value among the hardness value of all samples due to the existence of silicon, intermetallic compound and fine grains. Each of parameters separately influences the hardness result. Silicon promotes beta phase formation with BCC crystal structure which has limited slip planes at room temperature. The precipitation of intermetallic compound at the grain boundaries leads to hindrance of dislocation movement. In the presence of fine grains in material, they are available in many grain boundaries which acts as an obstacle against dislocation movement [100]. The reason of having high hardness value for both reference samples are due to work hardening process which results from production of the brass by extrusion method. Plastic deformation occurred during extrusion method resulted in the hindrance of the dislocation movements. That case brings about increasing the strength of material [101].

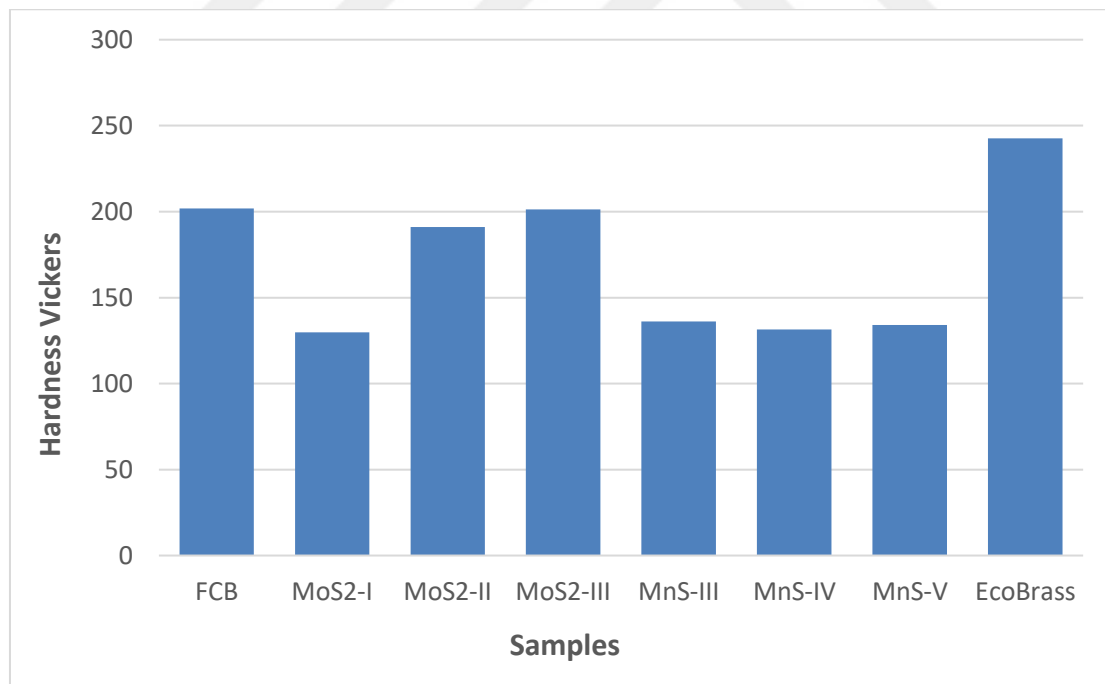


Figure 3.12 The Average Micro Hardness Values of All Samples

The hardness values of 5 different regions on the sample surface and its average hardness value for all samples were presented in Table 3.3. Hardness values of sample prepared with MoS₂ additives range from 130 HV to 202 HV. When the hardness values of the

samples were compared among themselves, MoS₂ added brass samples were found to be highest hardness value. As the content of the silicon addition increases, the hardness value of the samples increases. Furthermore, silicon solely precipitated at the grain boundaries or formed in the interface between the two phases (alfa and beta phases.). There are no significant differences in the hardness values of the brass materials produced with MnS additives when compared with themselves. When the hardness values of the samples prepared with MoS₂ additives were compared, MoS₂-1 had the lowest hardness of the sample prepared by MoS₂ additives because of the Widmanstättén microstructure and low beta phase fraction. Among other prepared samples, MoS₂-3 sample has the highest hardness value due to existence of beta phase and intermetallic compounds. On the other hand, increasing the amount of silicon resulted in promoting the formation of the beta phase brings about increasing wear of tool tip. Moreover, the hardness values of the MoS₂-3 sample produced by the casting method have a similar hardness value to F.C.B, which is produced by thermomechanical process.

Table 3.5 Microhardness measurement results for all samples

	Microhardness test results (HV)					
Samples	1	2	3	4	5	Average
FCB	186.00	210.20	196.40	216.90	199.60	201.82
EcoBrass	234.90	243.30	239.00	254.10	242.20	242.70
MoS ₂ -I	149.20	128.60	126.20	129.60	115.10	129.74
MoS ₂ -II	213.20	219.50	154.10	163.30	204.80	190.98
MoS ₂ -III	208.20	201.50	204.80	210.20	181.50	201.24
MnS-III	150.70	124.60	141.50	129.10	135.10	136.20
MnS-IV	125.50	123.00	144.50	152.00	153.50	141.50
MnS-V	140.40	131.00	124.60	145.70	159.00	139.14

3.4.2 Tensile Strength

In this part, the effect of additives on ultimate tensile strength and elongation in new generation brass alloys will be reported. Figure 3.13 and 3.14 present ultimate tensile strength and elongation of samples. The range of ultimate strength in all samples is in between 270 MPa and 570 MPa. MnS-5 has exhibited the lowest tensile strength and elongation among both prepared samples and reference samples (FCB and Ecobrass) because of having intense columnar dendrites which bring about deteriorating of mechanical properties due to showing anisotropic mechanical properties which facilitates intergranular segregation in the microstructure. Higher volume fraction of beta phase for Ecobrass has led to the highest tensile strength with 570 MPa value and exhibited moderate elongation with 22.24 %. Beta phase gives good hot workability for the matrix and improves its quasi-static strength and also has typical features such as higher hardness and ultimate tensile strength but lower elongation at room temperature [102].

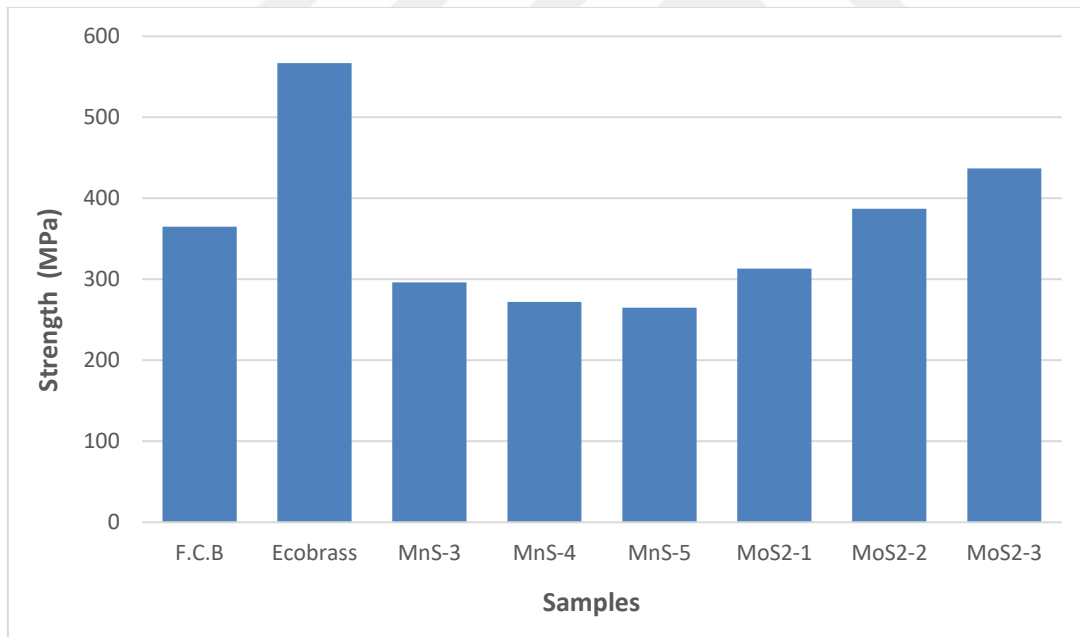


Figure 3.13 Comparison of the result of average ultimate tensile strength values for all samples

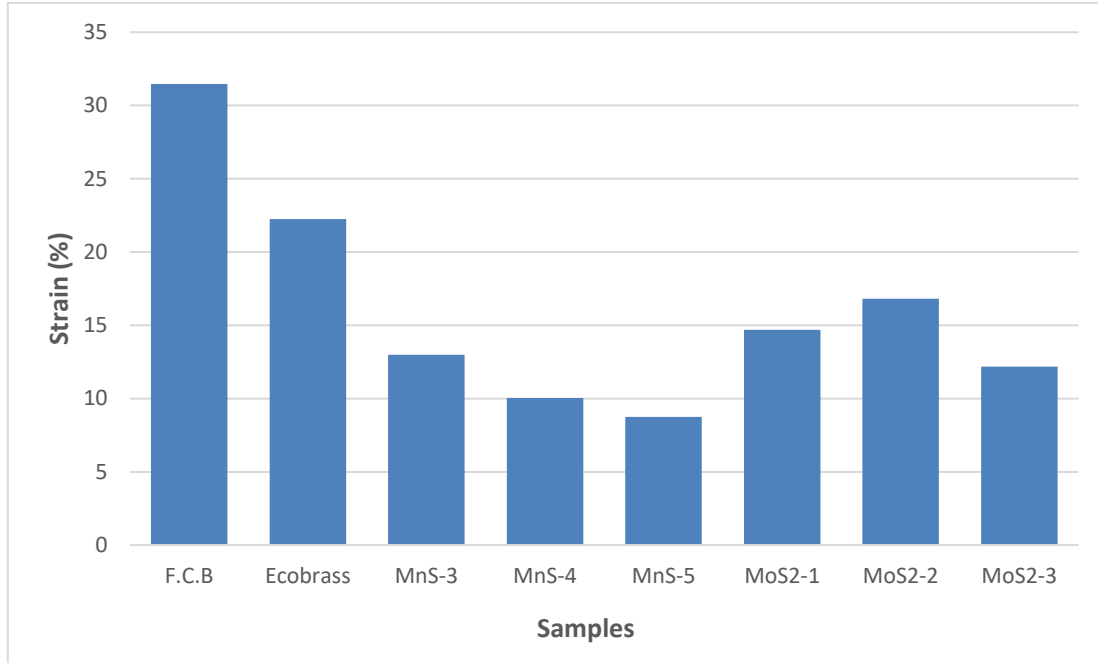


Figure 3.14 Comparison of the result of strain values for all samples

Many reasons can be attributed to the fact that the samples produced by casting process exhibit a much lower mechanical behavior in terms of both tensile strength and elongation compared to reference samples which were experienced thermomechanical process

Firstly, the microstructure of MnS added samples consists of dendritic structure which have many micropores and includes segregation. Secondly, MoS₂ added samples have brittle phase such as beta phase and several inter metallic components precipitated at grain boundaries in the microstructure. Finally, commercially available reference samples (FCB and Ecobrass) have undergone thermomechanical processes such as extrusion or rolling to reduce grain size and minimize microstructural pores and segregation.

The ultimate strength and elongation of both MnS-4 and MnS-5 do not satisfy minimum requirements of service conditions due to not reaching limit values according to EN 12164 standard in industrial applications, but this can be fixed by heat treatment process such as precipitation hardening. With increasing silicon contents for MoS₂ added samples, the ultimate strength has increased but elongation behavior did not exhibit consistent or compatible results since each sample has a different morphology. MoS₂-2 sample has higher elongation value because of the existence larger beta grains in microstructure but exhibited moderate ultimate tensile strength when compared to MoS₂ -1 and MoS₂-3 samples. This case was also emphasized in the previous study [103].

3.4.3 Fractographic Examination

Fracture surface examination of samples after tensile test was conducted using SEM technique using under secondary electron mode as shown in Figure 3.15. The fracture surface of FCB is a typical example of ductile fracture mechanism which has many dimples with various size and depth, and develop in three stages as nucleation, growth and coalescence of micro-voids. The outer of ring has relatively smooth surface when compared to center part in SEM image for Ecobrass. In addition to that, isolated cracking with depth and coarse size formed by existence of IMC's particles. The micro voids in outer ring of Ecobrass is smaller than the ones in center region owing to low hydrostatic pressure [104]. Tree-like structures on the fracture of MnS-3 is generally exhibited dendritic structure which is formed by solidification process after casting. In this situation, the nucleation and growing of crack begins in the tip of dendrite because this region acts as stress raiser. It is known that dendritic structure is a casting defect and includes many porosities in its microstructure. The combination of intergranular and transgranular cracking are observed in the fracture surface of MoS₂-4. This fracture mechanism incorporates a specific failure mechanism which includes both brittle cleavage fracture and ductile fracture with coalescence of micro-voids. The initiation of crack is provided by coalescence of micro-voids; however, ultimate failure resulted by cleavage. IMC's precipitated along grain boundaries can lead to crack formation and propagation in brass matrix. Besides, this circumstance may be accelerated by the environmental conditions and corrosive effect. Each sample has exhibited different fracture mechanisms due to their microstructure. Especially, the presence of non-metal inclusions can bring about larger void nucleation and also causing cleavage fracture due to incoherence with brass matrix prior to plastic deformation [105]. The shear face indicates brittle character and is ascribed to shift to low ductility behavior by the existence of dominant beta phase in the microstructure [106].

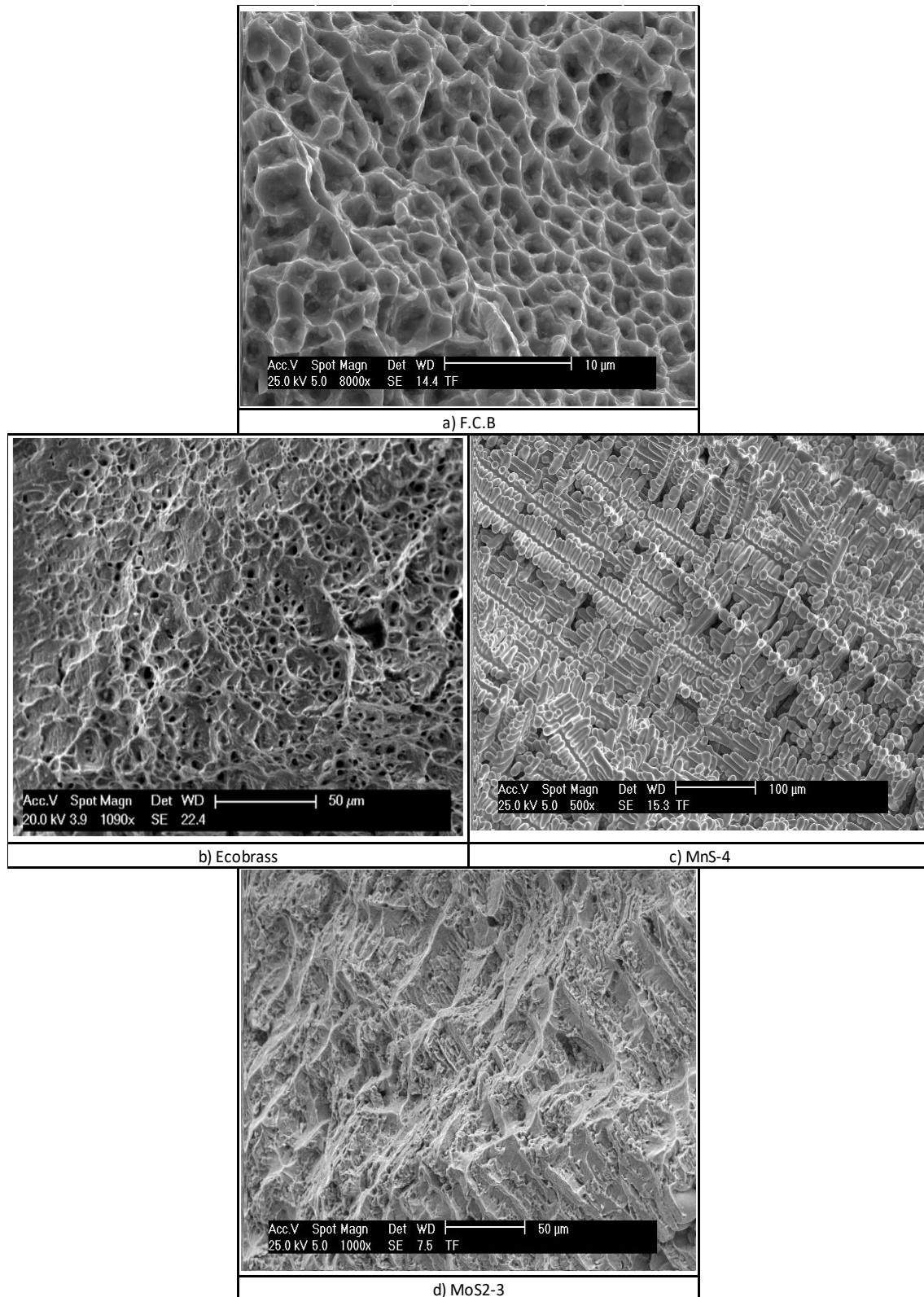


Figure 3.15 SEM pictures and comparison of fracture surface for a) F.C.B , b) Ecobrass, c) MnS-4 and d) MoS₂-3 after tensile strength test.

3.5 Chip Formation and Morphology

After machining processes, chips were collected to evaluate machinability of prepared and reference samples, because chip formation is one of the most common criteria to determine machinability characteristics. Due to two reasons, chip formation is considered as an important criterion:

- The chip swells around the spindle that leads to the milling machine become dysfunctional.
- The disposed fine chips that come out during machining process are placed in the mechanical and electrical components of the lathe and make the device dysfunctional.

Since high efficiency and productivity are important factors in industrial applications and production, machining parameters are determined according to the maximum performance of the lathe. According to trial-and error experimental studies and the parameters commonly applied and reported in the literature were used as machinability parameters. Table 2.5 presents machinability parameters applied in this study for all samples.

According to the reports of Copper Development Association Incorporation, the brass material has both higher machinability character and lower tool tip wear. In addition, it has superior surface finish quality in terms of aesthetics. Therefore, the power and robustness of the latest high-speed machine tools and the shops have the capacity to increase the rates of extracting brass workpiece materials in milling, drilling and turning operations [107].

In this section, chip formation of all samples is examined according to ISO 6385-G1 by evidence of photographic image after machining process. Disposable chips are light and have small chip dimension for all samples. Figure 1.13 shows the classification of commonly observed chip formation types according to ISO 6385-G1. This table assists to classify chip formation in terms of both shape and size. Materials having high index in machinability is generally attributed as type of 4th, 5th and 6th in Table 2.5.

Both the continuous and discontinuous chips are constantly contact between rake and flank edge during machining process. This leads into vibration which increase surface

roughness on surface between the swarf and tool. In addition, that lead to trigger accentuated wear on tool tip. [108]

Machining chip size and shape of all samples observed in this study were shown in Figure 3.16. The chip size and the shape reveal that they differ from each other in both reference samples and the prepared samples. In Figure 1.13 the chip formation of FCB reference sample is elemental formation shown in eighth image after machining process; on the other hand, chip formation of Ecobrass is compatible with loose type in Table G1.

Microstructural changes or phase transformation play a significant role and the type of addition of alloying elements or compound materials have strong influence that can alter or modify for different shape and size of the chip type during machining processes [109]. Furthermore, chip formation is significantly affected by phase distribution in brass matrix [64]. As can be seen in Figure 3.16, the increase of the additive materials causes only shortening of the length of helical chips but does not change chip formation. It was found that increasing additives has not distinctly changed chip thickness of prepared samples. The micrographs of optical and scanning electron microscope were used for examination of chip thickness ratio for samples. The alpha and beta duplex phases detected by XRD analysis from sample prepared with MnS additives (depicted in Figure 3.1) have excellent chip-breaker properties. Chips formed from all MnS additives have the structure shown in 4th image in Figure 1.13. The chip of sample prepared with MnS-3 additive is formed in short helical chip shape. This type of chip formation has also been compatible for sample prepared with MnS-5 additive, but it is shorter. Chip formation for MnS-4 did not clearly match with chip type in accordance with ISO 6385-1975E-G1. It is partly compatible with washer-type helical chip formation. The chip formation of the samples prepared with MoS₂ are slightly different from those prepared with MnS additives. MoS₂-1 samples are in the short tubular chip form like sample prepared with MnS-3 due to alpha Widmanstätten precipitation and the chips of MoS₂-2 and MoS₂-3 samples correspond to the arc chip with loose form due to increasing silicon contents in alloys because of the presence of beta phase.

The flow of the chip depends on the tool interface and the mechanical properties of the work material and notably affects the chip morphology [110]. Significant variations were obtained concerning the mechanism of chip forms. The optical photograph images taken

from longitudinal cross sections of chips produced from external turning under the same machining parameter conditions are shown in Figure 3.17. As examined in chip forms of FCB reference samples, chip morphology is related to fragmented form. They appeared as “saw tooth” or “closed- separated saw-teeth”. A great deal of chips fragmentation appeared in FCB chips due to lower plastic deformation in cutting region [58]. Since lead considerably reduces friction and chip thickness ratio in cutting zone, chip formation of Ecobrass wholly compatible with saw-tooth formation and not separated like FCB and MoS₂-3 samples. Chips morphology were observed for MoS₂-1 and MoS₂-2 formed with serration or tooth-like appearance. The more separated for each tooth in serration the highest chip fragmentation takes place eventually. Thus, the serrated chips turned into the fragmented chips.

Samples prepared with MnS additive have a lamellar chip morphology which is frequently accounted for shear bands deformation which promotes micro-cracks in alpha/beta interface. Due to the higher amount of ductile alpha-phase, high chip thickness ratios were determined for samples prepared with MnS additives. Since not having enough additives content friction is higher at cutting region and appeared distortion trace in microstructure of chip surface for MnS-3 and MnS-4 samples clearly. Comparing of lead-free brass MoS₂-3 sample according to chip morphology exhibited same behavior in leaded brass alloy (FCB) sample. The presence of phases and its distribution could influence chip morphology of prepared sample. MnS added brass samples with higher alpha phase in their microstructure lead to lamellar chip formation which resulted from homogeneous deformation whereas, saw-teeth chip formation appeared in MoS₂-3 sample, owing to inhomogeneous deformation, which took place by abundant beta prime phase and IMCs in its microstructure. Samples prepared with MnS additives have saw teeth form while MoS₂ samples have exhibited regular saw teeth form. When machinability is evaluated in terms of microstructure, MoS₂-1 and MnS-3 have Widmanstättten precipitates which reduces critical strain to commence shear band formation during machining process [94]. When machinability is evaluated in silicon alloyed brass, discontinuous chips were formed due to existence of various brittle phases (β , χ , η and κ) depending on additives amount [111].

The processes that the material has undergone previous such as rolling, extrusion and heat treatment or process conditions substantially influences chip morphology. The hardness values of FCB, Ecobrass and MoS₂-3 samples were above the average (see Table 3.3). Some parameters such as the phase fraction and their distribution in the microstructure can affect the chip morphology. This case was emphasized in the previous study [94].



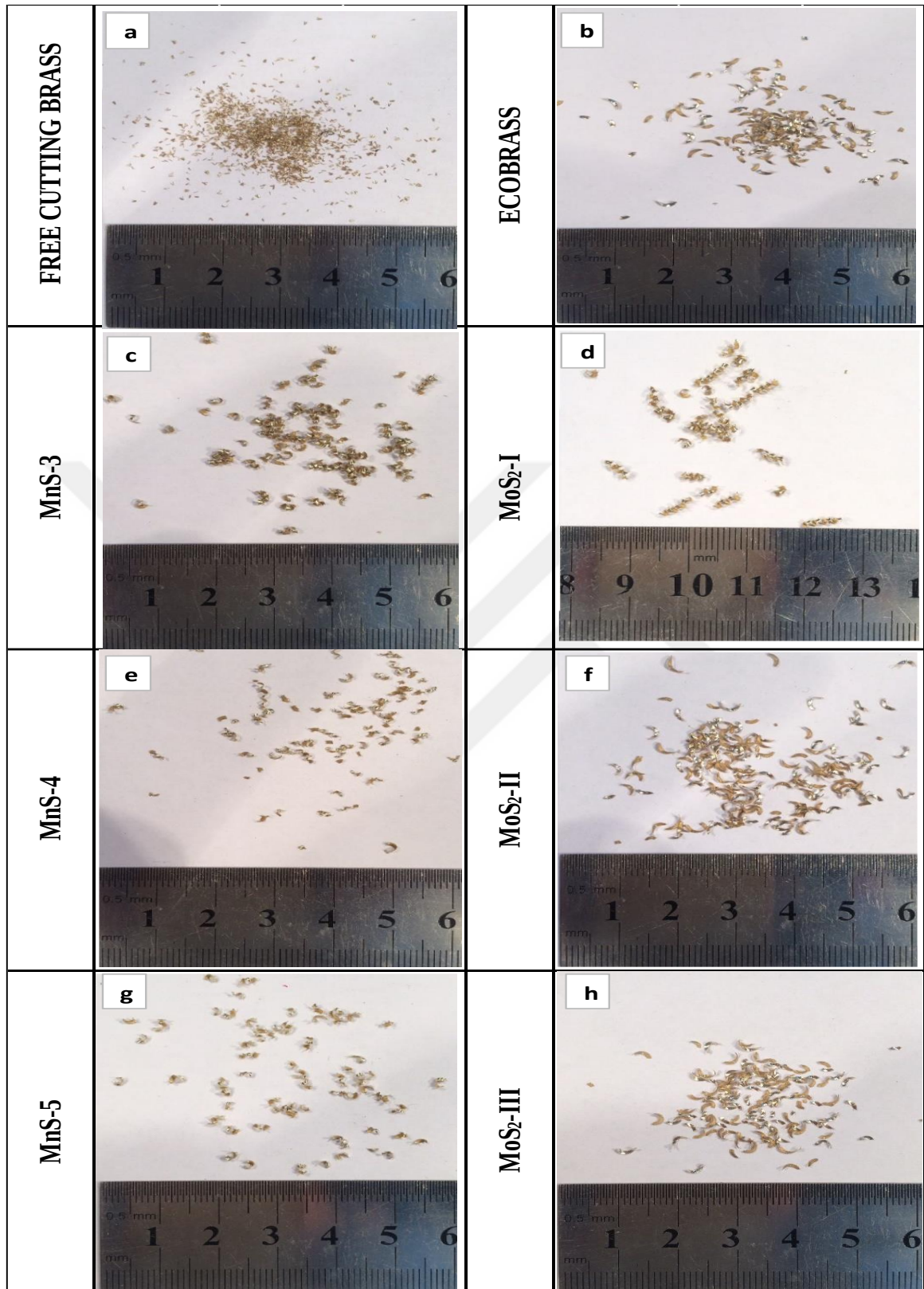


Figure 3.16 Macrographs and comparison of chip types for a)F.C.B b) Ecobrass, c) MnS-3, d) MoS₂-1, e) MnS-4, f) MoS₂-II, g) MnS-5 and h) MoS₂-III

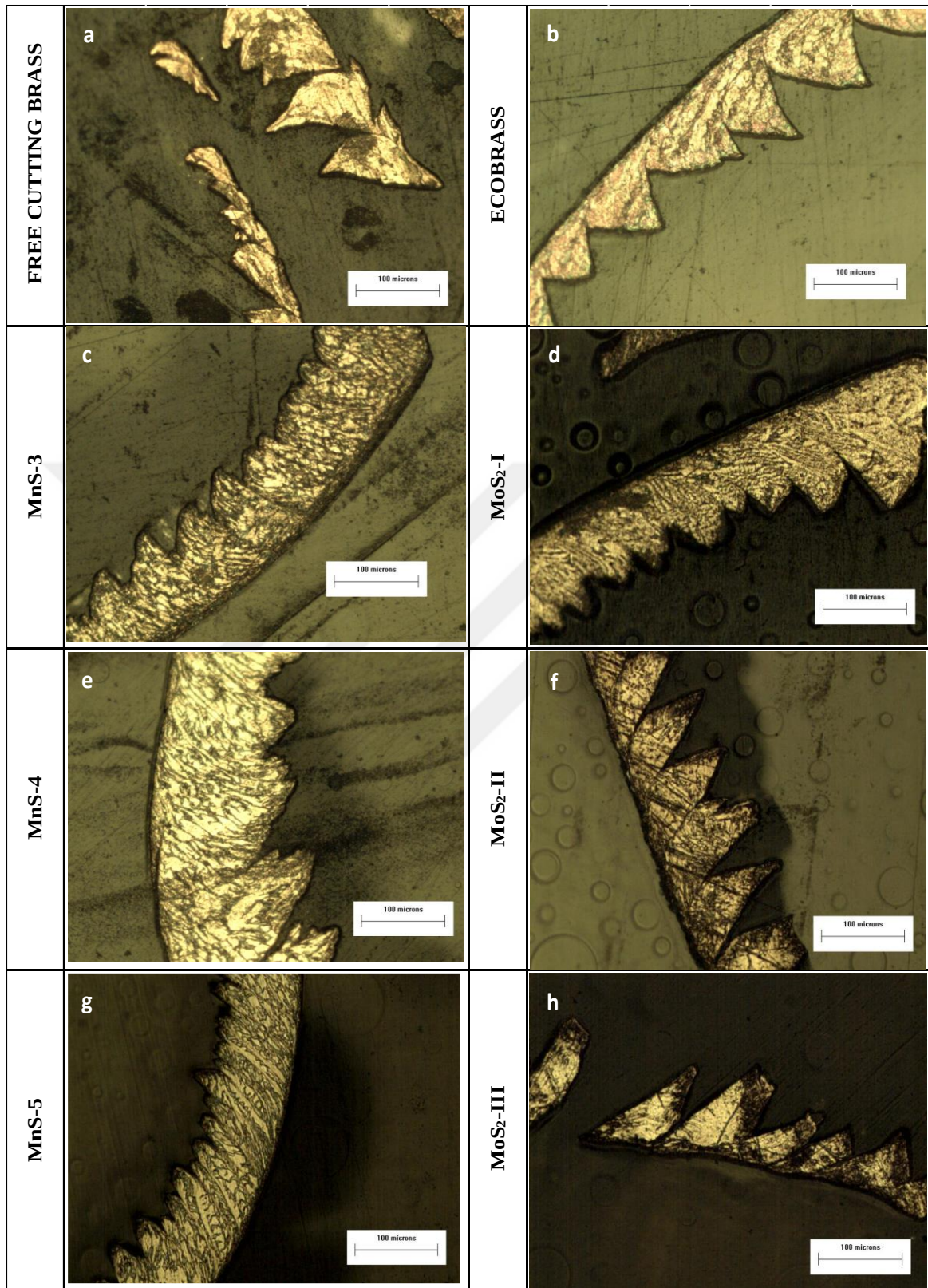


Figure 3.17 Optical microscopy images of chip formation for a) F.C.B b) Ecobrass, c) MnS-3, d) MoS₂-1, e) MnS-4, f) MoS₂-II, g) MnS-5 and h) MoS₂-III at x.100 magnification

Figure 3.18 shows SEM micrographs to determine chip morphology of samples. There are many cracks and traces of crack propagation on contact surface for chip morphology of Ecobrass which resulted from inhomogeneous deformation due to beta phase and fine size IMC's. These cracks on the sawdust like surface can be linked to the behavior of brittle materials under tension. Serration chip forms with discrete segment of about 10 μ m in thickness for FCB reference sample (Figure 3.18-b). Flatty smooth surface which takes place by shear motion of two neighbor fractured surface on chip surface during machining process are noticeable and, related to ductile fracture surface features. There are various chip shape surface regions such as free surface, contact surface between chip and tool, shear surface and fracture surface were denoted by A, B, C and D characters, respectively for MnS-3 sample. (in Figure 3.18-c. The difference in width from one end of the chip to the other end is remarkable. The width of head part on chip is about 200 μ m but tail part is about 530 μ m. This is due to the fact that no other sawdust is separated from the tail of the sawdust. Figure 3.18-d shows free surface part on chip for MnS-4 sample closer. The value of surface roughness is lower by the fact that it resembles a smooth zigzag form. It appears that serrated components are taken place distinctively on a fragmented chip forms for MoS₂-3 sample in Figure 3.18-e, furthermore; slip surface and undeformed surface has been come out in chip surface formed with lamella formation On the other hand, high-density cracks are abundant on the chip surface of both FCB and Ecobrass bring about traces of concave and cavity hence increasing the surface roughness values. Lower plasticity has resulted in smooth regions on the shear surface and fracture surface during machining process. The presence of secondary phases, inclusions, and the other irregularities (many interfaces in matrix) induce stress concentration in microstructure [112]. Therefore, this case promotes void formation and improves void growth in shear bands. Crack is formed with the development of void growth that connects to each other. This case triggers off to form fracture on interface between chip and tools [113].

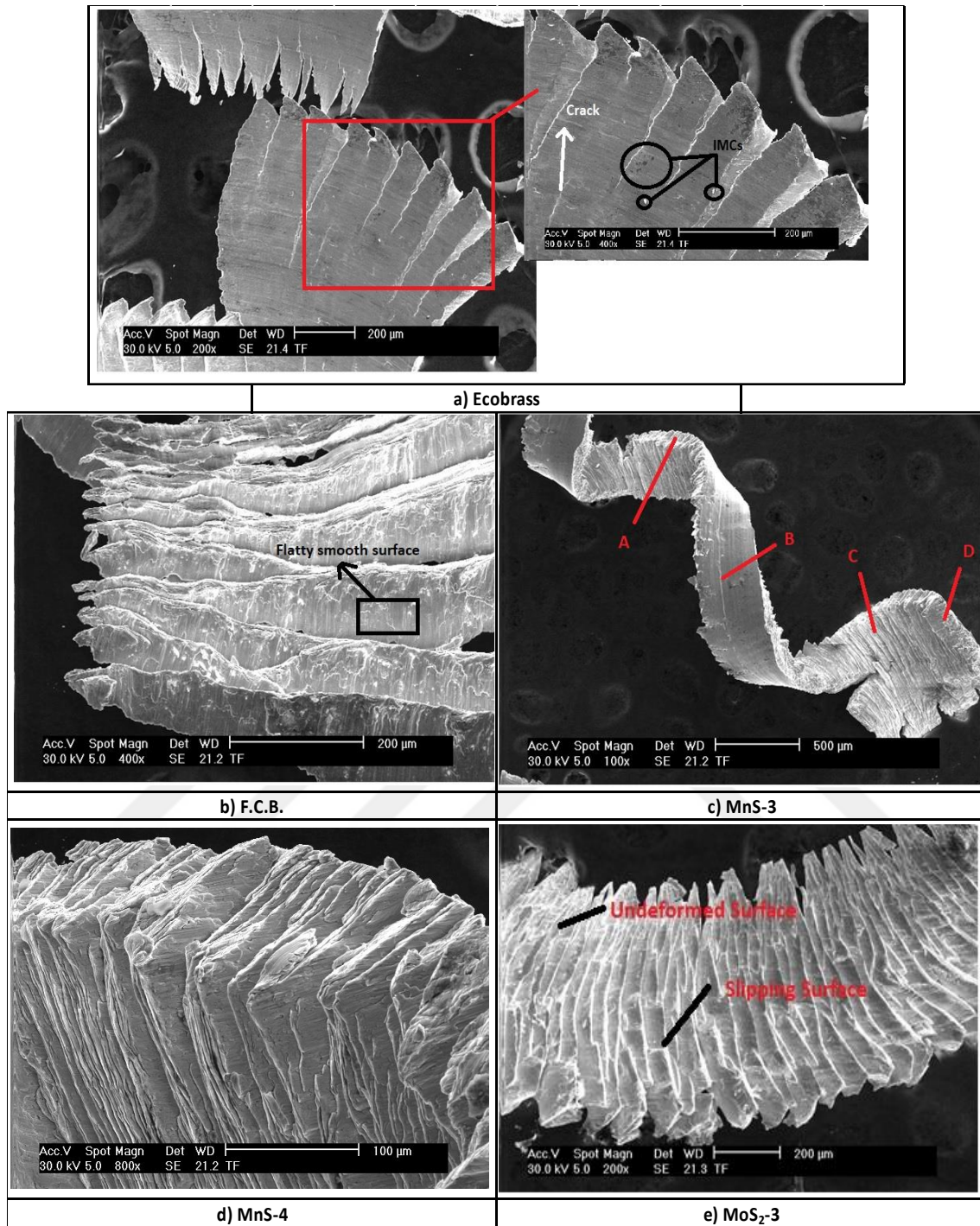


Figure 3.18 SEM images of chip surface morphology a) Ecobross , b) F.C.B, c) MnS-3, d)MnS-4 and e) MoS₂-3

3.6 Surface Roughness

In the industrial scale, surface roughness is an important criterion for machinability. Peripheral surface of samples takes place in chills zone due to rapid cooling. Since this "chill zone" does not reflect the real mechanical behavior of the samples, the part of this

zone was removed as chip by turning operation and then machinability test has been performed.

In Table 3.6, the surface roughness values of the samples evaluated according to the machinability parameters of Table 2.3 are presented. The surface roughness values of the prepared samples and reference samples range from 0.63 μm for MoS₂-3 to 2.25 μm for F.C.B. All of the prepared samples have a lower surface roughness than the reference samples. The lowest surface roughness values were obtained from samples prepared with MoS₂ additives due to its lubricant properties which account for low coefficient of friction and its layered structure [114]. The increase in MoS₂ addition further reduced the surface roughness value. MnS additive shows lubricant properties to some extent compared to MoS₂ additive. It can be seen that the surface roughness value of sample prepared with MnS additives enhanced but was not influenced much with increasing additive content into base alloy.

Table 3.6 Surface roughness values for all samples

Samples	Surface Roughness Value Ra (μm)					
	1	2	3	4	5	Average
F.C.B	2.21	2.23	2.36	2.49	1.94	2.25
EcoBrass	1.99	1.70	2.08	1.89	2.30	1.99
MnS-3	2.03	1.18	1.29	1.42	2.10	1.60
MnS - 4	1.35	1.54	1.68	1.38	1.53	1.50
MnS - 5	1.74	1.52	1.51	1.52	1.70	1.60
MoS₂-I	1.52	1.23	1.12	1.88	1.03	1.36
MoS₂-II	0.60	0.93	0.62	1.05	0.62	0.76
MoS₂ III	0.57	0.52	0.59	0.80	0.67	0.63

Figure 3.19 shows the average surface roughness values for all samples. As the previous study underline, strain hardening which has occurred on the surface of sample during

machining process influences the surface roughness because each material has different deformation ability [115]. However, in this study, the presence of alloying elements and the phase distribution have a considerable effect on surface roughness rather than this case. It was observed that the increase of MoS₂ additives in brass alloy leads to a decline in average surface roughness value. In addition, increasing Si alloying element content in brass resulted in higher beta volume fraction in microstructure and led to increase in the surface roughness. In other studies, it was emphasized that the increase of beta phase had a positive effect (increase) on surface roughness [54].

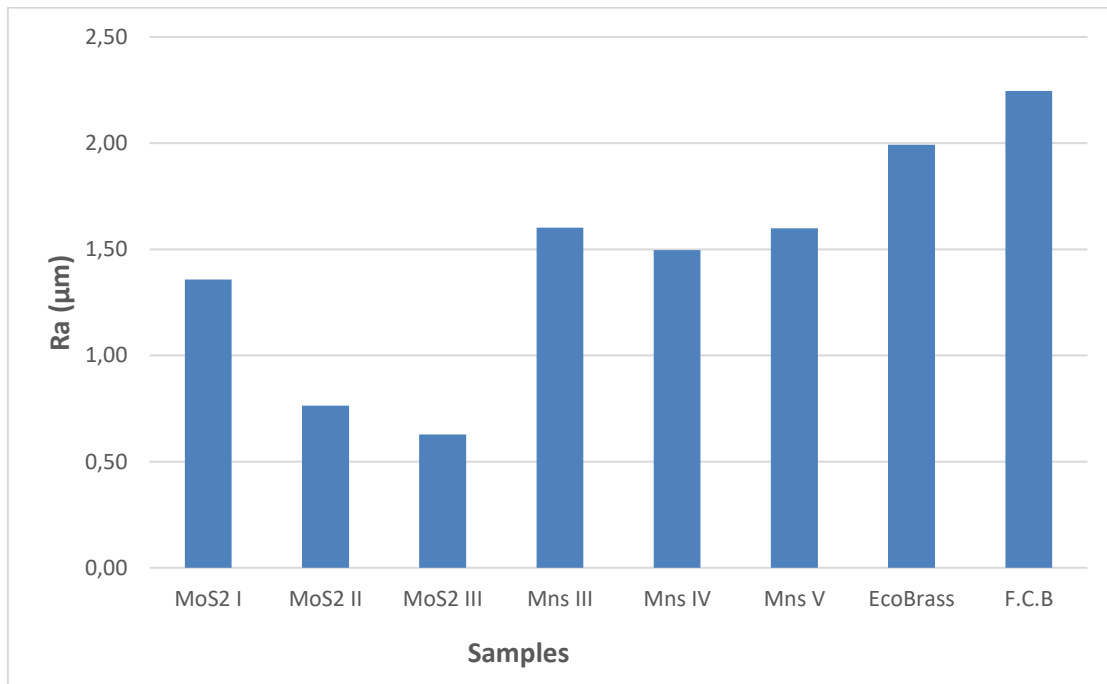


Figure 3.19 Average surface roughness of all samples

The other parameter which affects surface roughness value is hardness. As the addition of additives increasing into brass, this could promote the fraction of beta phase which is brittle and has a higher hardness value when compared to alpha phase in brass matrix. Thus, roughness value of machined surface decreases and also a smaller size of chip and chip thickness are achieved because of having brittle characteristic [62]. The existence of MoS₂ in brass microstructure significantly affected and reduced the surface roughness value which lead to very smooth and polished like shiny surface after turning.

3.7 Zinc Equivalent

Most common additives formed with solid solution in matrix lead to deviation of reactions on Cu-Zn diagrams and binary copper-zinc equilibrium diagram no longer applies. For this reason, Guillet zinc equivalent rule is used to determine fraction of alpha and beta phases. The formula is described with X% symbol as given below [64]:

$$X\% = \frac{C_{Zn} + \sum C_i K_i}{C_{Zn} + C_{Cu} + \sum C_i K_i} \times 100 \quad \text{Eq. 3.2}$$

C_{Cu} : Cu content in brass

C_{Zn} : Zn content in brass

C_i : The sum of additives content in brass

K_i: Fictitious zinc equivalent value of additives

The chemical composition of prepared sample including various additives by as-casting process listed in Table 2.3. The fictitious zinc equivalent value of Si, Al and Sn elements which significantly influences the reaction on binary Cu-Zn diagram and existence of phases on microstructure; are 10, 6 and 2, respectively [55]. Zinc equivalent values calculated using Guillet's conversion equation are shown in Table 3.7 in this study. Furthermore, the values in table just predict the existence and distribution of microstructure phase and might not be accurate due to non-equilibrium solidification.

Table 3.7 Chemical composition corresponding to zinc equivalence and phase components

	Zinc Equivalent Values % (χ)	Phase Components
MnS-3	38.22	α , β' and IMC
MnS-4	39.65	α , β' and IMC
MnS-5	39.88	α , β' and IMC
MoS₂-1	40.55	α , β' and IMC
MoS₂-2	42.04	α , β' and IMC
MoS₂-3	45.24	α , β' and IMC

The addition of Si promotes formation of β -crystals and suppresses α nucleation in liquid brass alloy during solidification. This leads to formation of duplex phase even in low zinc content for prepared samples, thus their microstructure changes from single alpha phase to duplex phase. Sn and Al have similar effect to Si element in the microstructure of the brass alloy.

The increase in the addition of Sn to the brass alloys causes the drag of the peritectic reaction direction to a low Zn content as well as taking place at a low temperature. However, it has been reported by other researchers that the addition of Si into brass change the position of reaction to lower Zn content at higher temperature [94].

Initially, the zinc equivalent is used to estimate the phases of cast brass alloys. It helps to predict whether brass alloys contain as single alpha phase or duplex phase. The estimated phases in Table 3.7 based on Guillet's conversion equation consistent with the results of microstructural characterization.

For example, when the content of brass alloy which is 15 wt. % zinc, 3 wt. % silicon, 6wt.% tin and 5 wt.% aluminum, is produced in a brass production factory, its zinc equivalent is calculated as 46 wt. %

3.8 Stress Corrosion Cracking

Stress corrosion cracking is quite common failure in brass materials depending on the service condition. This failure results from attacking aggressive corrosion environment and stress assists in growth of cracks in microstructure. According to the previous study, it has been determined that dezincification corrosion occurs during stress corrosion cracking in brass materials in ammonia environment. [108]. Chemical composition, grain orientation, distribution of phase and precipitates has remarkable influence on the susceptibility of stress corrosion cracking [119]. Figure 3.20 shows micrograph of samples after being immersed in a mixture of ammonium chloride and hydrogen peroxide aqueous solution to determine resistance of stress crack corrosion. Except for the sample prepared by MnS additives, no cracks were found on the surface of the samples in the stress corrosion cracking testing. Unlike the others, the microstructure of sample prepared by MnS additives consists of columnar dendrite structure which includes many defects such as porosity, segregation (typical casting structure). Based on these findings, it is thought that the MnS added sample is susceptible to stress crack corrosion.

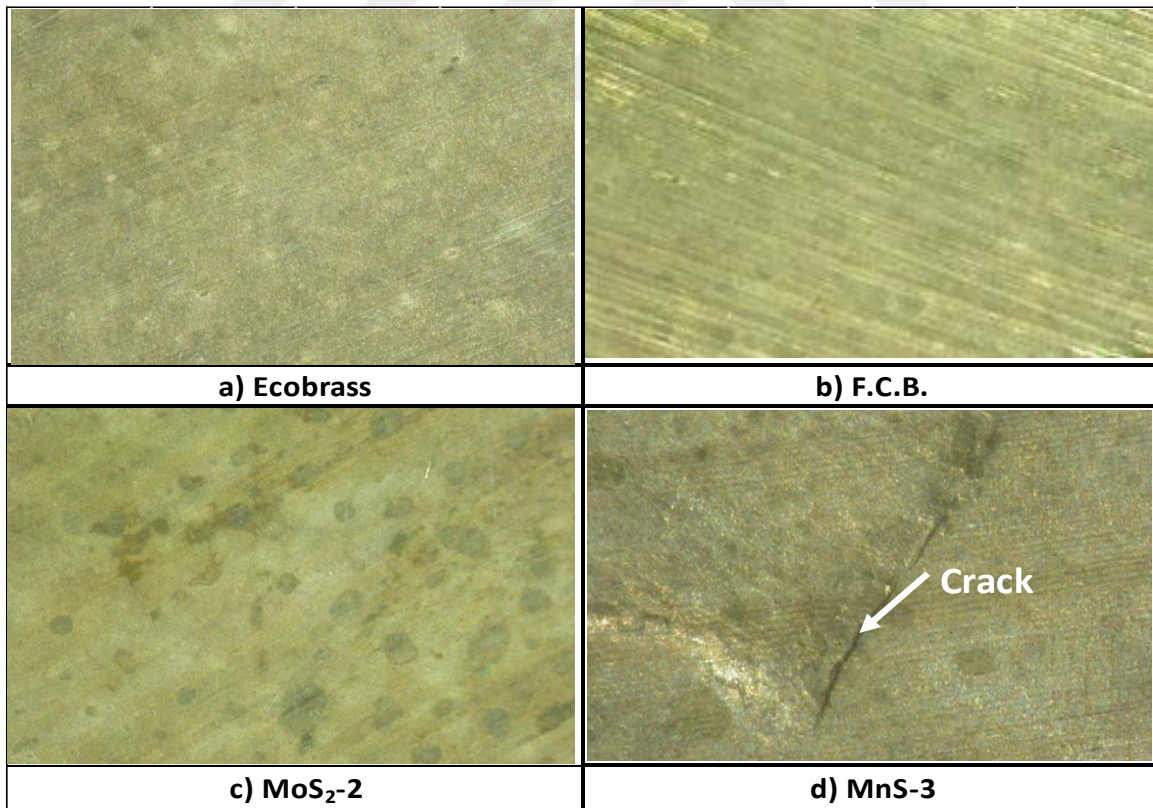


Figure 3.20 Microstructure images of samples a) Eco brass, b) F.C.B. c) MoS₂-2, d) MnS-3 taken by a stereo microscope after stress corrosion cracking test

3.9 Dezincification

It is known that brass alloys containing β phase are more susceptible to dezincification corrosion due to the high zinc content (over 20 % wt. zinc). According to reported study in the literature, the mechanism of dezincification is based on two fundamental aspects. Copper and zinc acts as a galvanic cell in the initial stage which causes preferential dissolution of zinc in the solution. Another aspect is a formation of Cu_2O porous layer on brass surface bring about decreasing current density. This case leads to dissolution of copper and zinc, followed copper re-deposition on the surface of sample. [120]. In order to prevent dezincification in brass, selected alloying elements such as arsenic, niobium should be dispersed into the microstructure to form a protected layer which is dense and unbreakable structure on the surface of brass alloys that can act as a shield to protect attacking by chloride ions.

When a metal is immersed in an electrolyte, the open circuit potential is measured without applying voltage and current in order to determine stability of potential in an electrolyte. This potential requires to be measured prior to the electrochemical testing because OCP (open circuit potential) shows the thermodynamic tendency of metal in an electrolyte solution. The values of O.C.P as a function of time in aqueous solution of CuCl_2 for reference samples (FCB and Ecobrass) and samples prepared with MnS additives are shown in Figure 3.21. As it can be illustrated in Figure 3.21 for potential value of all samples except Ecobrass sample almost exhibits stagnation behavior with over time. In the first 50 seconds of the potential of the Ecobrass sample, it moves in the positive direction and then becomes stable. This case is due to the oxide protective layer which forms on the surface of Ecobrass sample in the initial 50 seconds. O.C.P of the FCB sample has shifted in the negative direction in the first 100 seconds. Then it has reached a stable potential value again with a slight rise. This behavior distinctly exhibits the breakdown of oxide layer on the surface of FCB and dissolution of FCB. After that potential of FCB increases in the positive direction over time by virtue of formation oxide layer. The open circuit potential values of the samples prepared with the MnS additive exhibit the same behavior. The potentials of the samples prepared by MnS addition were overlapped on the graph. No potential change was observed during measurement. That means MnS containing samples retain their corrosion resistance.

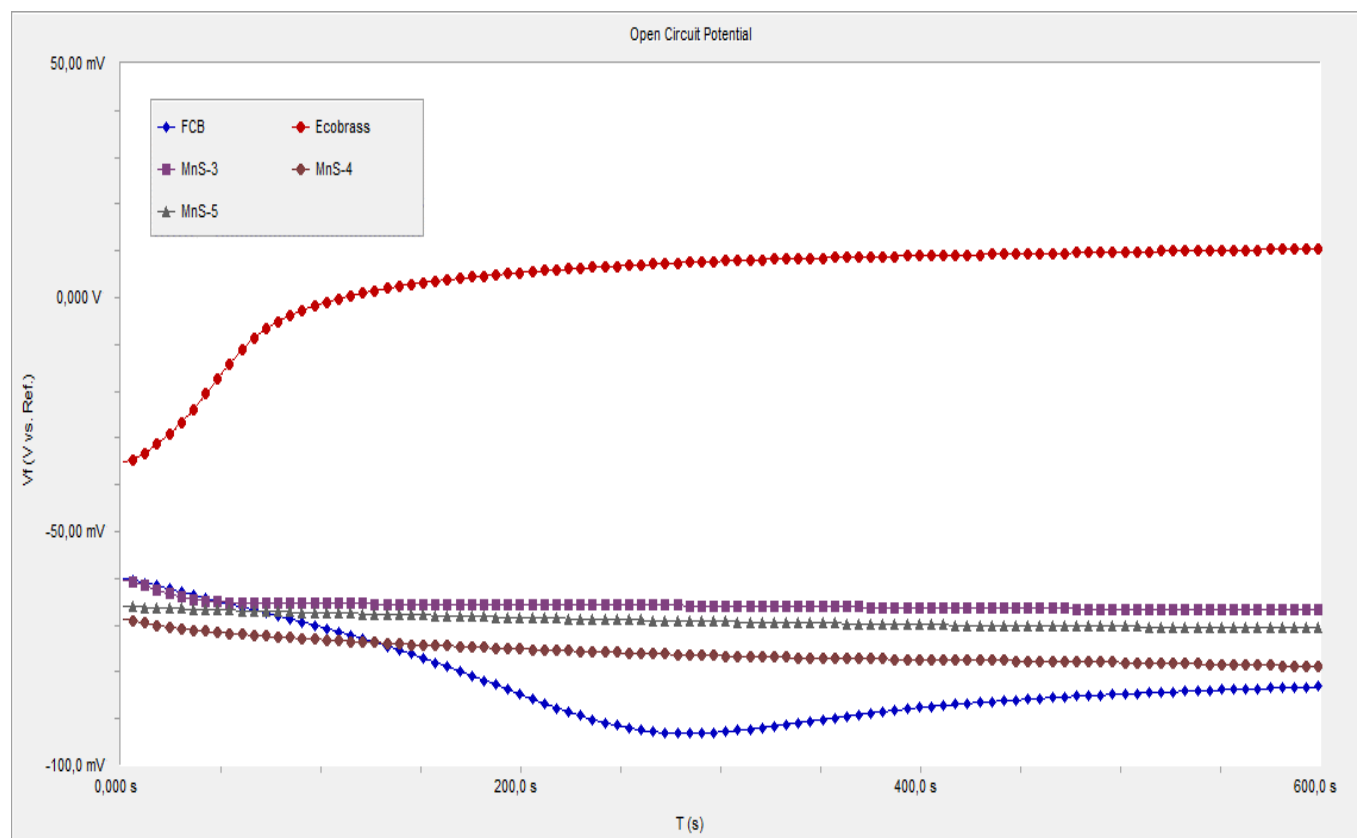


Figure 3.21 The O.C.P. curves of reference samples and sample prepared with MnS additives

Figure 3.22 presents open circuit potential of the sample prepared with MoS₂ additives and reference samples in aqueous solution of CuCl₂. The potential behavior of FCB and Ecobrass samples are similar as mentioned above in Figure 3.21. Potential values of the sample prepared with MoS₂-1 has exhibited different behavior from the others. In the first 30 seconds, the potential of the MoS₂-1 slightly increases then the potential remains constant in following 200 seconds. After 250 seconds, the potential value falls back to -65mV levels and reaches the potential value of MoS₂-2 and MoS₂-3 samples.

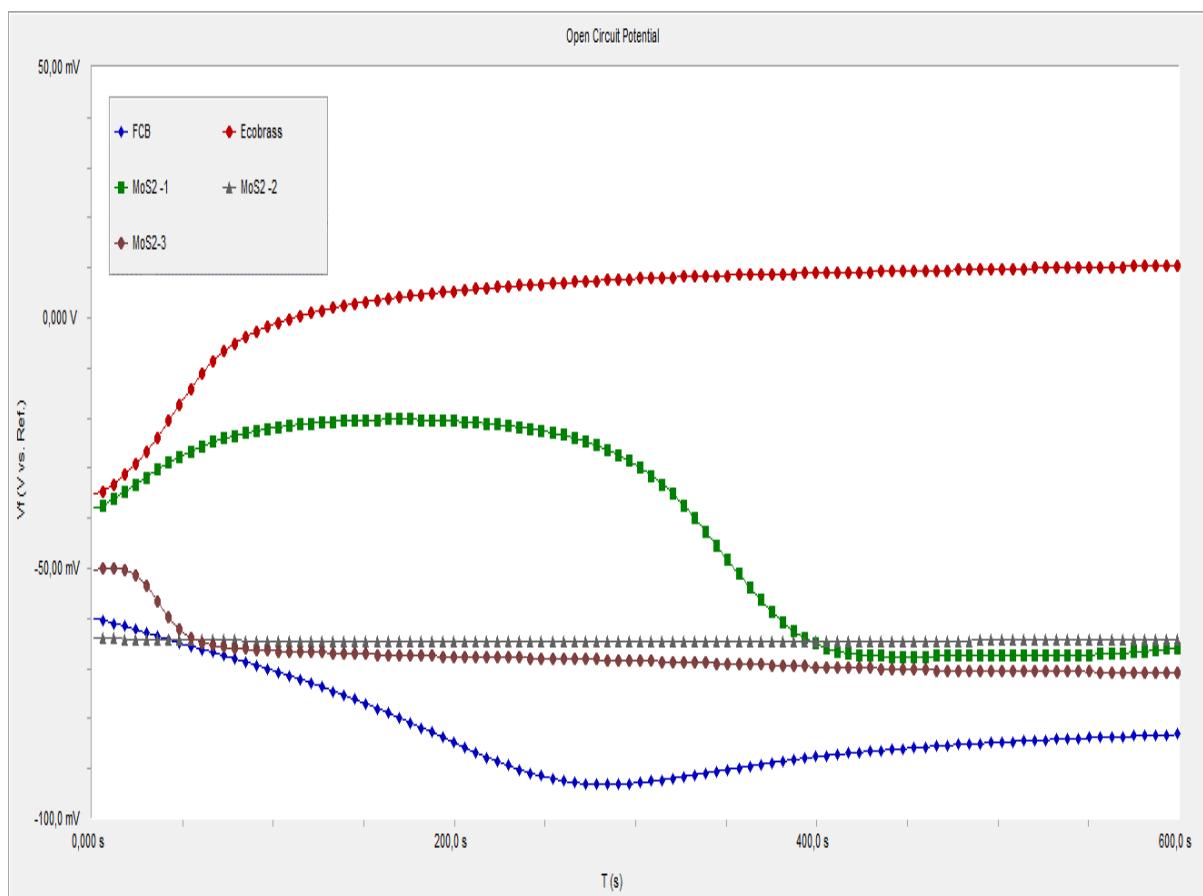


Figure 3.22 The O.C.P curves of reference samples and sample prepared with MoS₂ additives

The polarization curves of sample prepared with MnS and MoS₂ additives and reference samples are shown in Figure 3.23 and Figure 3.24, respectively. These graphs consist of three distinct regions which are active-passive transition region, active region and cathodic limit current region. In contrast to polarization curve of Ecobrass sample, polarization curves of all samples generally exhibit the same behavior on cathodic polarization sites. From the polarization curve of the Ecobrass sample, it is understood that the corrosion reactions take place in the activation control, because their graph acts as a region of ohmic polarization. In high potential, Ecobrass sample exhibited cycle of cathodic reaction kinetics. In anodic sites, polarization curves of MoS₂-1 and MoS₂- 2 samples partially act as passive region due to the complex oxide layer which dissolves into solution then creates itself with an increased potential. This case indicates that oxide layer does not have a stable behavior. Behavior of polarization curves for the rest of the samples are under passivation control due to large curve for anodic (β_a) side in Tafel slope. This case is observed in the sample prepared with MnS additives under low current

values. The corresponding current value of the active-passive region on the polarization curve decreases with the increase of MnS addition. It can be said that the addition of MnS makes the oxide layer more stable and the corrosion resistance of the samples enhanced.

Table 3.8 Potentiodynamic polarization values for all samples after dezincification test.

Samples	BetaA (V/decade)	BetaC (V/decade)	Icorr (mA)	Ecorr (mV)	Corrosion Rate (mpy)
FCB	10.65	-5.101	16.34	-63.90	439.67
EcoBrass	10.835	-3.157	10.83	-32.20	412.45
MnS-3	20.108	-10.061	6.43	-32.30	258.45
MnS-4	24.736	-10.037	4.48	-30.30	313.42
MnS-5	18.148	-13.606	4.23	-25.30	334.22
MoS ₂ -1	26.32	-2.904	6.40	-39.90	383.63
MoS ₂ -2	3.269	-19.460	10.60	-31.40	159.88
MoS ₂ -3	3.595	-1.489	11.70	-36.40	136.54

The corrosion values of all samples from the polarization curves which was determined by the Tafel extrapolation method are given in Table 3.8. Corrosion potential (Ecorr) provides calculation of the corrosion current which gives rate of corrosion process. The anodic (β_a) and cathodic (β_c) Tafel slopes are used to determine corrosion potentials. Corrosion potentials and corrosion current values of the samples are close to each other except for FCB. The corrosion current value of FCB is highest among the corrosion current values of other samples, thus increasing the corrosion rate. The presence of discrete islets of lead observed by numerous studies suggest that these islets deteriorated the corrosion resistance and increased the corrosion rate due to the galvanic couple between lead and matrix [121]. Corrosion current and potential values of other samples are similar. As it can be seen in the Table 3.8, the lowest corrosion rate belongs to the MoS₂-3 sample. Reference samples have a lowest characteristic value among samples prepared by MnS and MoS₂ additives in terms of corrosion rate. The lower corrosion resistance of reference samples can be attributed (as shown in Fig. 3.25a) to the porous

copper oxide layer formed on the surface of them. The complex oxide layer formed on the surface of the samples prepared with MoS_2 has not stably act to protect layer (as shown in Fig. 3.23d); however, the corrosion rate of them have exhibited lowest value.

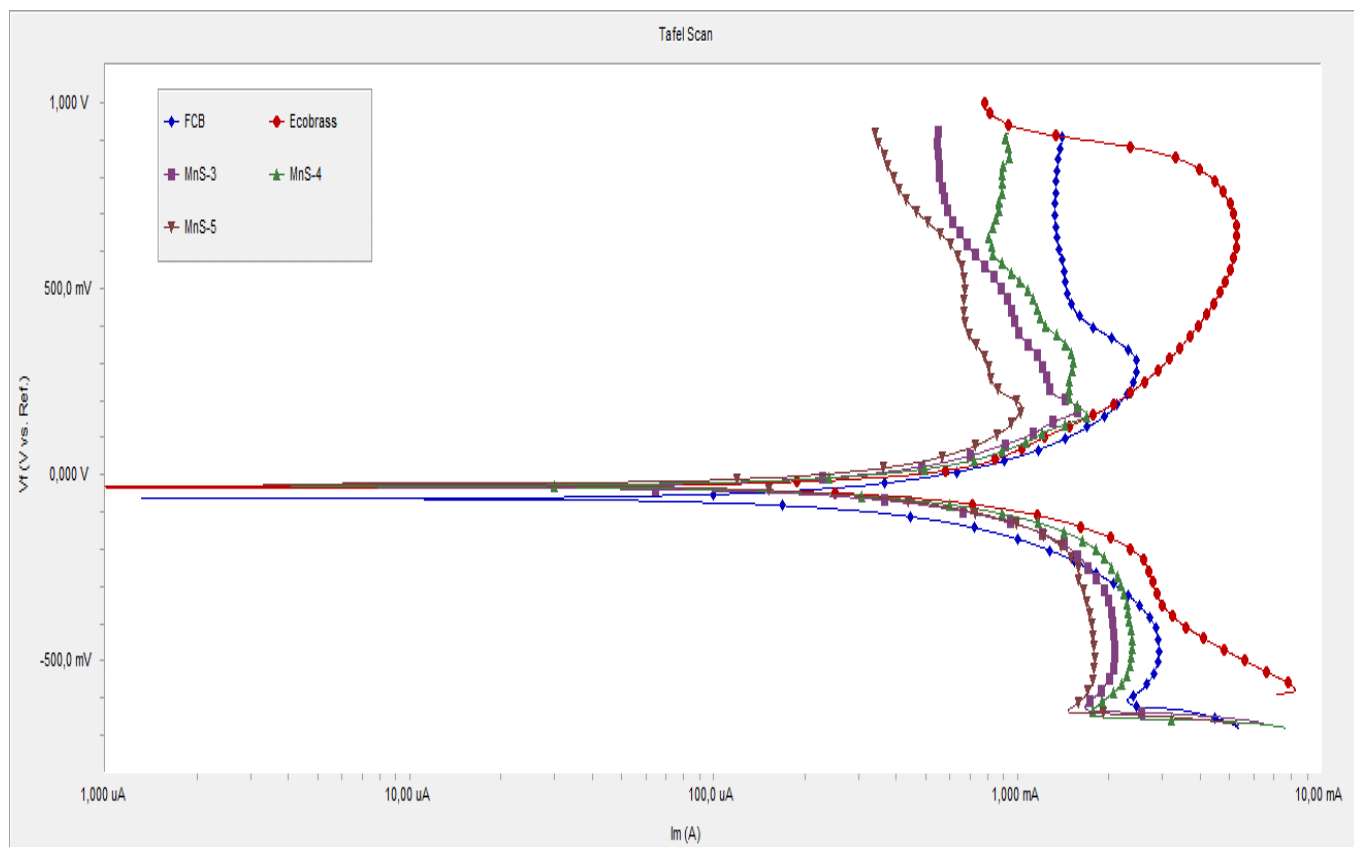


Figure 3.23 Potentiodynamic polarization curve of sample prepared with MnS additives and reference samples

Figure 3.25 shows the results of SEM-EDS and micrographs of SEM taken from the surface of the samples after the corrosion test for F.C.B, Ecobrass, MoS_2 -3 and MnS-5 samples. When SEM micrograph of Ecobrass reference sample (Figure 3-23 a.) is examined there is a thick layer constituting of cracks and pores which spread all over the surface of the sample after corrosion test. Peak intensities of zinc element were not found in EDS elemental analysis. This suggests that Ecobrass reference sample subjected to severe dezincification corrosion. Furthermore, attack of chloride ions on the surface brings about promotion of Zn dissolution and reduces the corrosion resistance of the sample.

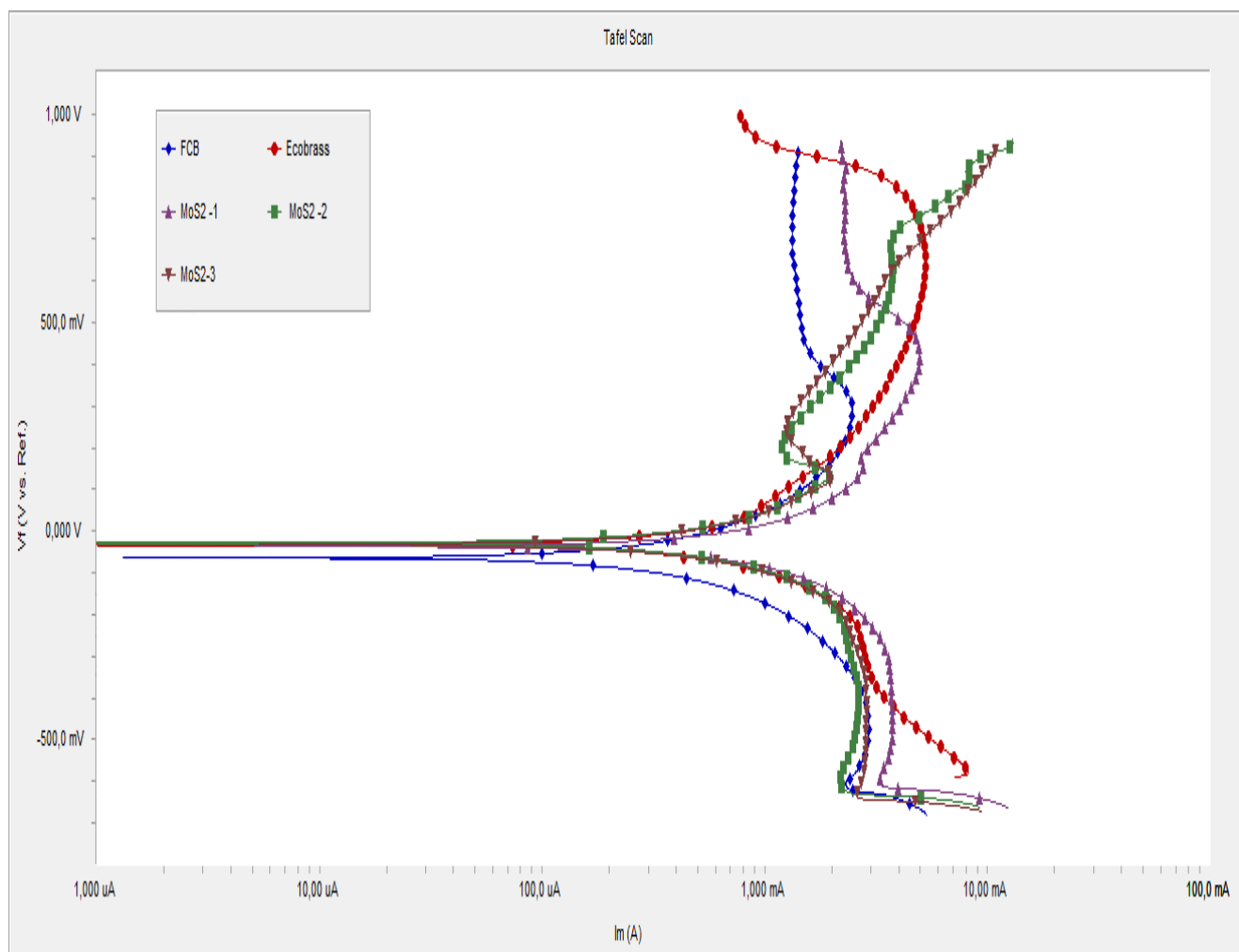
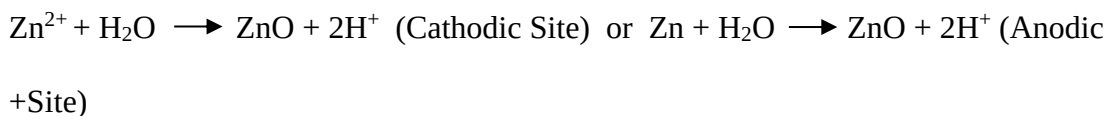


Figure 3.24 Potentiodynamic polarization curve of sample prepared with MoS₂ additives and reference samples.

The appearance of surface morphology on FCB sample surface is quite different from Ecobrass. The morphology of F.C.B. which contains, 3wt.% lead after corrosion test constituted a rough layer. This layer was formed by chlorine-containing corrosion products besides zinc oxide (ZnO) This result confirmed by SEM-EDS analysis and reported in a previous study [122]. From SEM-EDS analysis result, the presence of the element lead could not be determined due to leaching of lead, to the solution from outer surface of brass after corrosion analysis. A complex oxide layer structure with ZnO and Cu₂O was probably formed on surface of the sample.

Many studies reported [112, 113] both the anodic and cathodic reactions in chloride solution as outlined below:

Changing from zinc formation to zinc-oxide during corrosion process



For copper oxide formation



These oxide layers formed on the surface of the sample decreases dezincification rate via decreasing the current density. Trace amount of Sn was detected by SEM-EDS analysis. Previous studies [125] indicated that tin reacts with oxygen to form passive film which enhance the resistance of general corrosion on brass surface. Tin distribution in this passive film is not homogeneous, so the corrosion resistance is not stable as expected. The inner zone is rich in tin and the highest amount is at the corrosion layer/ metal interface thus being negligible amount in the outer surface. Samples prepared with MoS₂ and MnS additives having higher amount 2 wt. % of tin induced two different layer structures which are shown in Figure 3.25-c and d, respectively. Tin triggered formation of passive film layer which retards corrosion attack by both nucleation on alpha phase and propagation on beta phase as reported in a previous study [126].

In the elemental analysis method of the mapping of the SEM-EDS unit for MnS-5 and MoS₂-3 samples (Figure 3.26 and 3.27, respectively), the upper layer is rich in chlorine and the inner layer is rich in tin. The results of SEM-EDS analyses are in agreement with Beccaria's findings [123]. Aggregation of tin at the interface could hinder aggressive chloride ions from the brass surface by virtue of chloride ions being physically separated on porous copper structure [125]. Another implication is that there is a reduction in corrosion resistance with an increasing amount of silicon. Probably silicon is dissolved in solution with zinc and leaves a porous copper structure. As a result of dezincification corrosion test, it was observed that the corrosion rates of the samples prepared with MoS₂ decreased significantly. Based on the results of Figure 3.25-d and 3.27 SEM-EDS analysis, molybdenum element can be thought to form a protective layer.

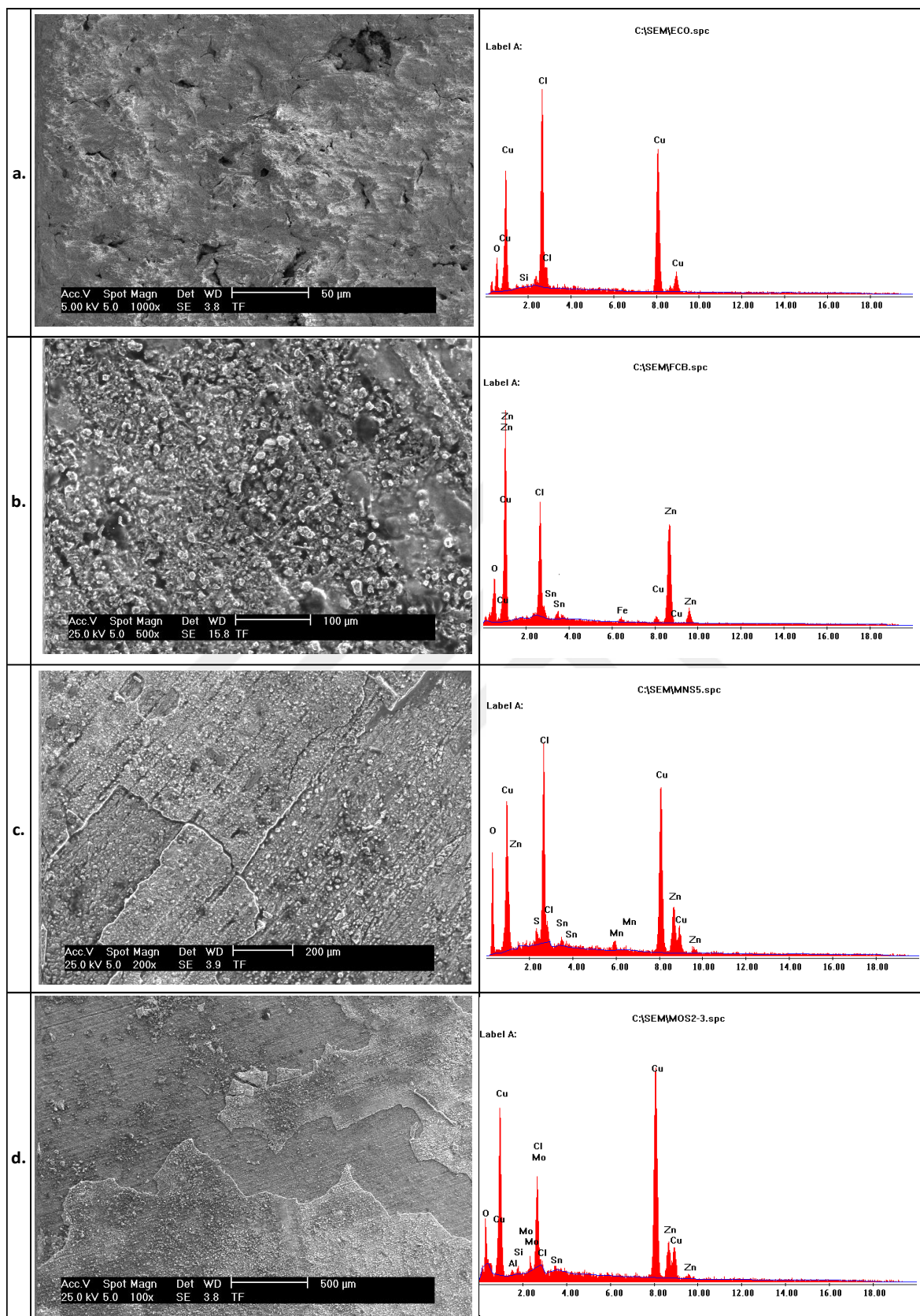


Figure 3.25 SEM micrograph and EDS spectrum from the corrosion surface of a) Ecobrass b) FCB c) MnS-5 and d) MoS₂-3 samples

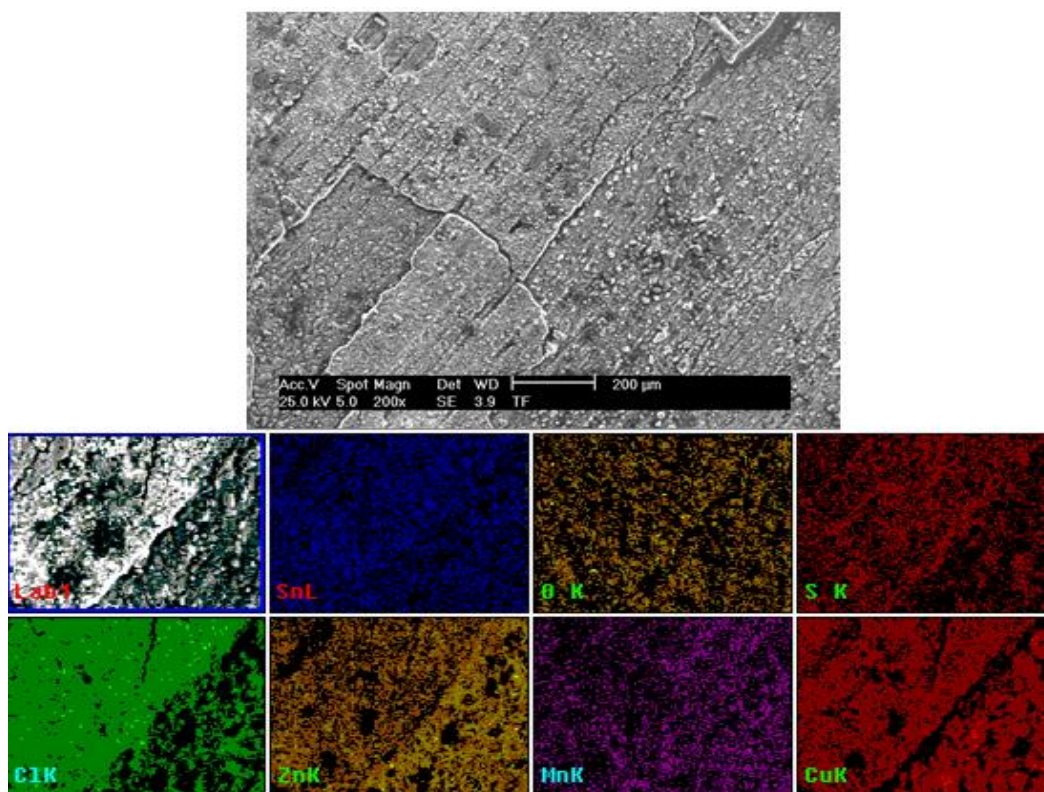


Figure 3.26 SEM micrographs with EDS maps of MnS-5 sample after corrosion test

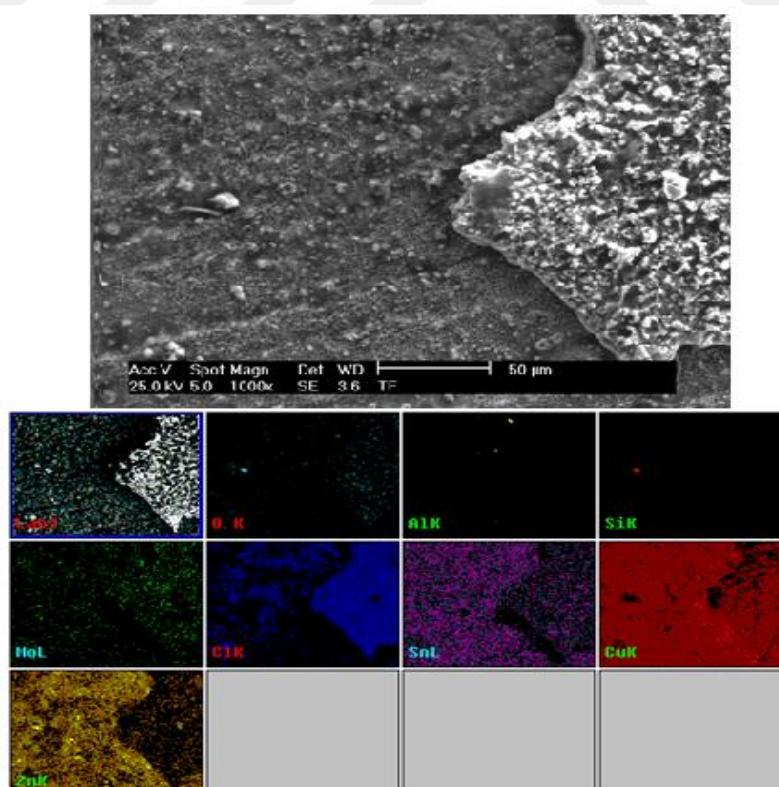


Figure 3.27 SEM micrographs with EDS maps of MoS₂-3 sample after corrosion test

3.10 Wear Test

The weight of samples after and before test, and percent of the weigh losses for samples are shown in Table 3.9. Weight loss between samples have not significantly detected. Thus, it is taken account to percent of weight loss to determine wear resistance. Ecobrass and MnS-4 have similarly exhibited weight loss behavior. From the view of percent of weight loss MnS-4 is higher than the others due the high existence of soft alpha phase. MoS₂-2 sample has the lowest weight loss by virtue of presence of hard and brittle beta phase.

Table 3.9 Weight loss and friction coefficient of samples during wear test

Weight (g)	Ecobrass	F.C.B	MnS-4	MoS₂-2
Before Wear Test	18.302	16.268	12.302	16.216
After Wear Test	18.298	16.265	12.299	16.214
Weight loss (%)	0.021856	0.018441	0.024386	0.012333
Average Friction coefficient (μ)	0.083076	0.067392	0.140889	0.014169

Figure 3.28 shows the variation of friction coefficient with time for selected samples. The friction coefficient values of each sample distinctively exhibited their characteristic depending on their different morphology and phase components. In initial step of analysis, the friction coefficient value of Ecobrass and F.C.B is 0.03 and these values have linearly increased to about 0.07 in 300 seconds. This characteristic behavior of friction coefficient for Ecobrass and F.C.B has attributed to brass film at the beginning of sliding process [127]. At the end of 400 seconds, the friction coefficient value has slightly increased to reach a value of about 0.1 μm for them and then have exhibited fluctuation behavior for 2000 seconds.

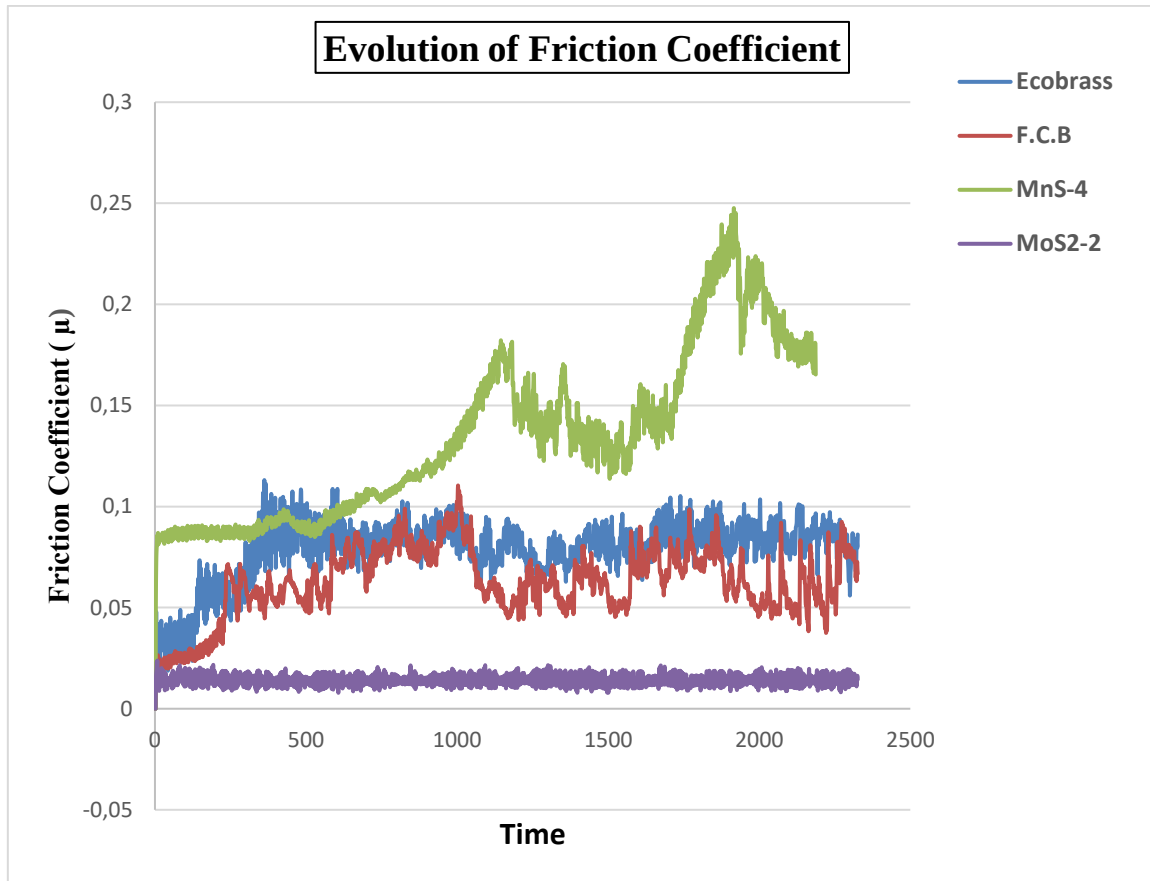


Figure 3.28 Variation of Friction Coefficient with Time

This fluctuation behavior in the friction coefficients is probably due to the phase distribution in the microstructure and variation of surface roughness as the time progressed [128]. It exhibits generally stable behavior. Curves plotted for MnS-4 has consisted of three steps. The first step, the friction coefficient has constantly risen; thus, remove particles by mechanical effect from the surface. The second fluctuation behavior suggests interaction between ball bearing and sample test material. The last one, casting defects in the microstructure such as micro porosity and segregation which can lead to increment of friction coefficient. The value of friction coefficient for MnS-4 is relatively highest among all test samples. The friction coefficient value of MoS₂-2 sample is approximately 0.01 μ and has not deviated along the test time due to the lubricant effect of MoS₂ structure.

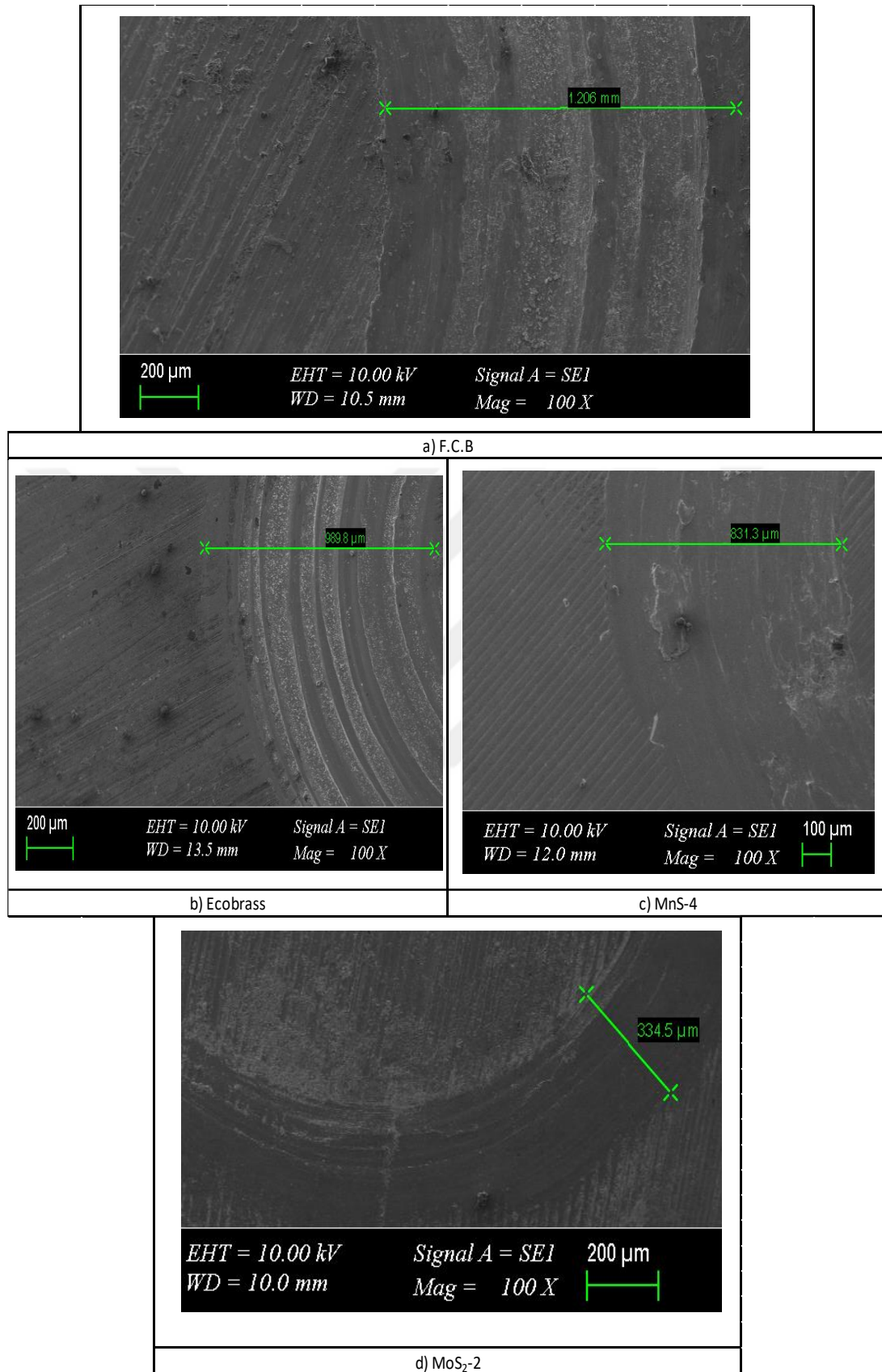


Figure 3.29 SEM images of worn surface a) F.C.B, b) Ecobross, c) MnS-4 and d) MoS₂-2

Figure 3.29 shows morphology of worn surface to get from SEM images for samples. Sliding tracks of which length is 1206 μm and, both large and small particles has been clearly observed on the wear surface of F.C.B sample. On the Ecobrass wear surface, the tracks are more severe and deep, but the track length of wear ring ball has decreased to 989.8 μm . The morphology of worn surface for MnS-4 has been exhibited different wear characteristic from the others sample due to having adhered debris and smearing surface. Beside it has observed with limited wear track of which length is 831.3 μm . The wear surface of MoS₂-2 has contained parallel scratches to sliding direction, and the track of wear ring ball which is 334.5 μm has lowest among the other samples due to its lubricant properties.

Wear mechanism of brass alloys mainly depends on their chemical composition, morphology, experimental conditions, hardness and roughness of sample [129]. In general, the wear mechanism is categorized into 3 groups as abrasive, adhesive and fatigue. The mechanism of the wear test samples in this study is abrasive type. Because the surface of worn samples has appeared to smear from rubbing surface instead of becoming slide marks due to transfer the sample to wear ring ball.

After the wear test to evaluate the wear mechanism of samples, microstructure of surface of samples were examined by secondary SEM images which were shown in Figure 3.30. During wear process, the pieces of metal are peeled resulting from friction surface. Peeled metal pieces which are harder have become oxidized or nitrides particles resulting from reaction of atmosphere. These particles may cause an abrasion type which have entrapped in between sample and wear ring surfaces. As wear process going on, hard oxidized particles lead to deep groove, fragmented debris and scratches on wear surface. This was emphasized in a previous study on wear behavior of brass alloys [130]. This observation was proved by SEM examinations of samples. Slip bands with smooth and slight traces was observed on MoS₂-2 samples. The existence of slip bands has identified as both abrasive and adhesive wear on surface of MoS₂-2 test sample.

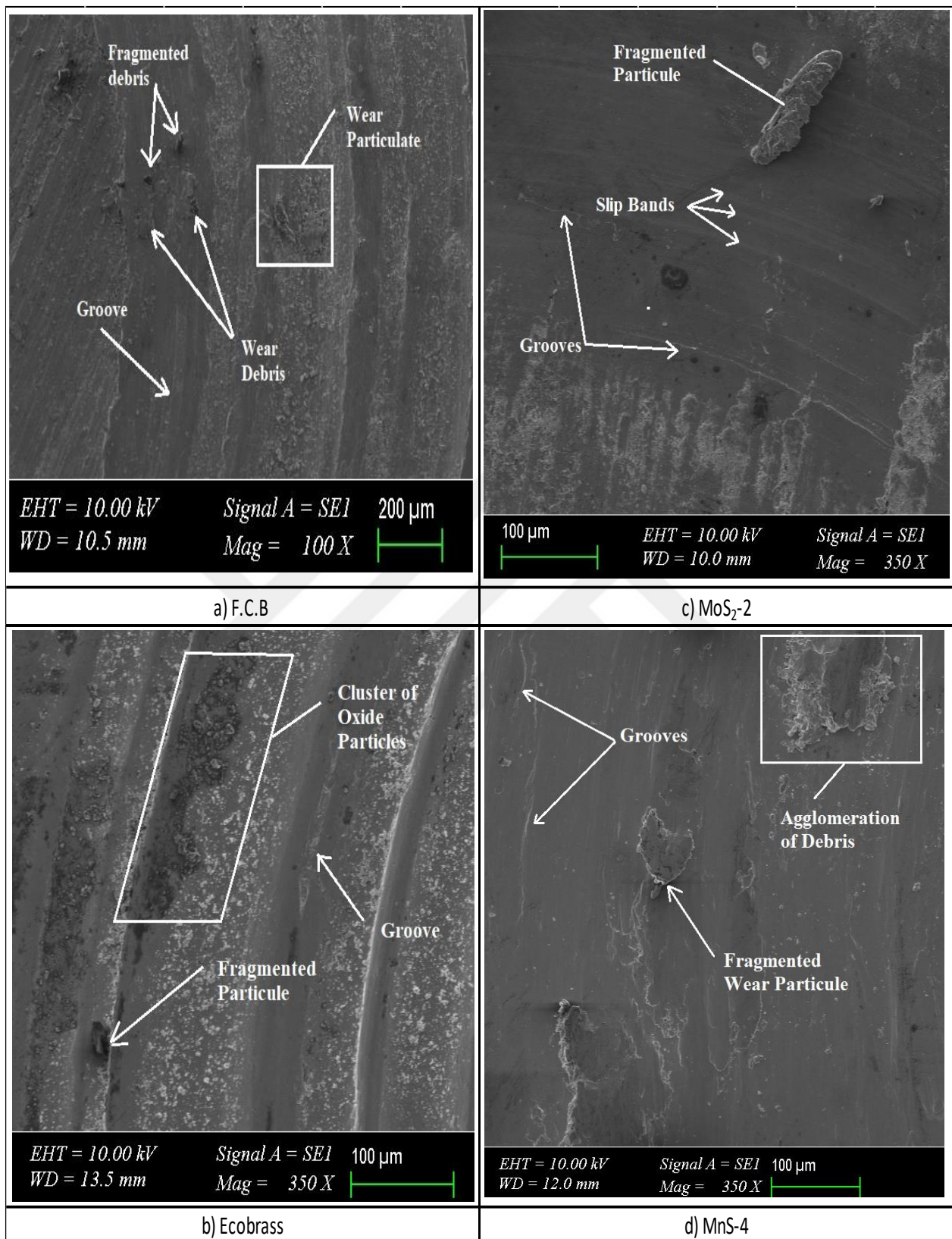


Figure 3.30 SEM observation of wear surface of samples a) F.C.B, b) Ecobrass, c) MoS₂-2 and d) MnS-4

4 CONCLUSIONS

The results of the addition of various additives into new generation brass were summarized and the conclusions drawn from this study were categorized into four groups which are namely characterization, machinability, mechanical, corrosion, and wear:

Characterization:

- Some microstructures revealed completely dendritic, some of them are Widmanstätten, some are only beta-phase and some of them are original brass as alpha and beta mixture.
- The addition of additives leads to small grain size and promote formation of beta phase; thus, bringing about increased hardness value of samples.
- It was observed that Si, Sn and Al additives promote beta phase formation in brass alloys and also resulted in variation of morphologies with increasing their contents in brass matrix.
- The microstructure and X-Ray diffraction analysis revealed that peritectic reaction has been shifted to lower zinc content by addition of Si and Sn in Cu-Zn phase diagram. Thus, the microstructure has transferred from duplex ($\alpha+\beta$) to single beta phase with increasing Si and Sn contents in brass matrix.
- Peak shifted on X-Ray diffraction pattern when Sn and Si additives located as a substitutional atom in crystal lattice induced stress rising fields in brass matrix.
- SEM images showed that Widmanstätten α precipitates and grows with acicular morphology inside grains and at the grain boundaries in microstructure of MoS₂-2 due to lower atomic mobility during solidification.
- Slag chemical analysis of brass alloys produced with MoS₂ show that some of MoS₂ has been detected from the slag and some may have turned into Cu₂S phase by peritectic reaction.
- Calculated zinc equivalent value of samples corresponding to phase components are compatible with the result of X-Ray diffraction and EDAX analysis. Especially, they are useful in predicting phase components in microstructure in non-equilibrium solidification.

Machinability:

- Chip formation influenced by the existence of hard and brittle phases in the brass matrix, as well as their distribution and morphology.
- Although the chip size of the samples prepared with MnS additives has the desired size and discontinuous chip form whereas the samples prepared with MoS₂ additives reveals promising and similar chip characteristics of F.C.B and Ecobrass.
- MoS₂ additive has the lowest surface roughness values due to its lubricant effect.
- Chip fracture mechanism depends on shear band formation and microvoids which are affected by the presence of hard brittle phase, IMC's distribution and size.
- One of the chip formations is type "C" shapes (loose) which is generally found samples having high beta fraction in the microstructure. Moreover, samples formed with helical washer type is based on dominant alpha phase.

Mechanical:

- All samples have brittle fracture surface; furthermore, sample prepared with MnS additives specifically do not fulfill ASTM B927 standards because of the presence of many flaws in the microstructure such as porosity, microvoids and defects caused by morphology of MnS-3 and MnS-4.
- The hardness values of the MoS₂-3 sample produced by the casting method which includes many defects and porosity has almost equal properties to F.C.B reference sample which was produced by thermomechanical process.

Corrosion:

- Tin addition provides protection against the oxidation in corrosive environment, on the other hand, silicon and zinc additions selectively lead to dissolution from microstructure due to their galvanic effects.
- After the corrosion test, EDS analysis was performed on MoS₂-2 containing sample revealing Molybdenum may have been reacted with oxygen to occur an oxide compound with a trace amount in microstructure during casting, thus acts as a protective layer against dezincification.

Wear:

- It was found that MoS₂-2 sample has the lowest coefficient of friction due to its structural and inherent lubricant feature.
- The presence of phase distribution and morphology in microstructure substantially affected the weight loss during wear process. MnS-4 sample has exhibited high percentage of weight loss because of the higher fraction content of alpha phase.
- Wear mechanism of brass alloys mainly depends on their chemical composition, morphology of the formed phases, experimental conditions, hardness and roughness of the samples. The dominant wear mechanism is adhesive type for all samples.

The test results of all samples performed in the thesis study are shown in Table 3.12. Based on these results, it was determined that the novel MoS₂-2 sample has the same or similar features of F.C.B and Ecobrass, both of which are currently used commercially in the industry. In addition, MoS₂-2 sample revealed promising corrosion behavior, better wear resistance and high surface roughness quality, outstanding lower friction coefficient and appropriate chip formation with comparable hardness and mechanical properties.

Table 4.1 Summary of experimental results for all samples

	F.C.B.	Ecobrass	MnS-3	MnS-4	MnS-5	MoS₂-1	MoS₂-2	MoS₂-3
Detected Phases	$\alpha - \beta' - \text{Pb}$	$\alpha - \beta' - \text{Cu}_4\text{ZnSi}$	$\alpha - \beta'$	$\alpha - \beta'$	$\alpha - \beta'$	$\alpha - \beta'$	$\alpha - \beta'$	$\alpha - \beta' - \text{IMC}$
Morphology	Alpha and Beta with Grains	Alpha and Beta with Fine Grains	Widmanstäetten	Widmanstäetten and Dendritic	Dendritic	Widmanstäetten	Coarse Beta Grains with α Widmanstäetten	Beta Grains
Hardness (HV)	201.82	242.70	136.20	141.50	139.14	129.74	190.98	201.24
Tensile Strenght (MPa)	365	567	296	272	265	313	387	437
Elongation (%)	31.47	22.24	12.98	10.03	8.74	14.96	16.81	12.18
Surface Roughness (Ra (μm))	2.25	1.99	1.60	1.50	1.60	1.36	0.76	0.63
Chip Formation	Elemental and needle chip form	Arc Chip with loose form	Arc Chip with connected form	Arc Chip with connected form	Arc Chip with connected form	Short Tubular Chips	Arc Chip with loose form	Arc Chip with loose form
Corrosion Rate (mpy)	439.67	412.45	258.45	313.42	334.22	383.63	159.88	136.54
Wear rate (%)	0.018441	0.021856		0.024386			0.012333	
Average Friction Coef. (μ)	0.067392	0.083076		0.140889			0.014169	

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