ÇUKUROVA UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES

MSc THESIS

Mete Han BOZTEPE

EFFECT OF BORONIZING TEMPERATURE AND TIME ON ABRASION AND CORROSION RESISTANCE OF AISI 1050 STEEL

DEPARTMANT OF MECHANICAL ENGINEERING

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We certify that the thesis titled above was reviewed and approved for the award of degree of the Master of Science by the board of jury on 25/08/2014.

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ABSTRACT

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In this study, tne effect of boronızıng temperature and tıme on abrasıon and corrosıon resıstance of AISI 1050 steel were investigated. Pack borozing process has been applied to AISI 1050 steel specimens at a temperature of 800-850 and 900 ºC with a time duration of 3-6 and 9 hours. Ekabor 2 has been used as a source of boron. The photographs of micro structures of boronized specimens have been taken and the layer thicknesses varied from 17 to 110 µm and the hardness values from 510 to 1890 HV have been obtained. These values have been compared with Taguchi method. Boronized and unboronized specimens have been subjected to abrasion test under the load of 30N by using sand papers which have grain size of 220 mesh. These specimens have also been sink into the 3,5% NaCl solution for corrosion tests in order to compare the corrosıon resıstance of specimens treated at different conditions.

Key Words: AISI 1050 steel, Boronizing, Corrosion, Abrasion

ÖZ

YÜKSEK LİSANS TEZİ

AISI 1050 ÇELİĞİNDE BORLAMA SÜRESİNİN VE SICAKLIĞININ AŞINMA VE KOROZYON DİRENCİ ÜZERİNDEKİ ETKİSİ

Mete Han BOZTEPE

ÇUKUROVA ÜNİVERSİTESİ
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: Prof. Dr. Necdet GEREN
: Prof. Dr. Birgül YAZICI

Bu çalışmada AISI 1050 çeliğinden imal edilmiş olan borlama numunelerine 800–850 ve 900 ºC'de 3–6 ve 9 saat sürelerle kutu borlama işlemi uygulanmış numunelerde borlama sıcaklığı ve borlama zamanın aşınma ve korozyon direncine etkileri incelenmiştir. Bor kaynağı olarak da Ekabor 2 kullanılmıştır. Borlanan numunelerin optik mikro yapı fotoğrafları çekilmiş borlama şartlarına göre 17 ile 110 µm arasında değişen tabaka kalınlıkları ve 510 ile 1890 HV arasında da sertlik değerleri elde edilmiştir. Bu değerler Taguchi yöntemi ile değerlendirilmiştir. Borlanmış numuneler ile borlanmamış numuneler 30N yük altında, 220 mesh tane boyutuna sahip kağıt zımparalar ile aşınma testi yapılmıştır. Ayrıca % 3,5 lık NaCl çözeltisine daldırılıp korozyon testlerine tabi tutularak aralarındaki korozyon dayanım farkları karşılaştırılmıştır.

Anahtar Kelimeler: AISI 1050 Çeliği, Borlama, Korozyon, Aşınma

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1. INTRODUCTION

Boron and boron products are being seen in daily life from kitchen devices to cleaning sector, drug sector. Boron and boron products are commonly used in glass and insulation products, fire resistance devices, detergents, automotive and air industry, agriculture, metallurgy, nuclear applications, construction and textile industry etc. But most commonly used in metal industry. In reactions they are being used as deoxidizer and removing gas.

Other application areas of boron are in some special alloying, making semiconductor, as a catalyzer device, strengthen in metal, ceramics and composites also in construction of nuclear reactors, as an additive material to concrete which has high density, also they are used as a control device to absorb neutrons in uranium-graphite batteries. Many important compounds of boron are being manufactured and used in different areas.

Boroning method which can be applied into ferrous based and nonferrous materials, also materials which are manufactured by powder metallurgy, is a thermo chemical surface hardening process. Because of heat effect in Fe and B atoms, there will be formation of FeB and Fe_2B in surface. As a result of formation of this compounds, there will be increasing in corrosion and wear resistance about 2100 Vickers hardness.

In this study, the corrosion and wear characteristics of AISI 1050 steel surfaces improved by various thermochemical heat treatments such as boronizing. Samples prepared from the test materials were treated at solid boronizing mediums. The hardness distributions, microstructures, wear and corrosion resistant studies were performed. The abrasion tests were carried out with pin-on-disc sample configurations and weight losses were determined as a function of sliding distance and applied load. The corrosion behaviours of tested samples were also examined to study the effect of boronizing on corrosion resistance of AISI 1050 steel samples treated at different contions.

2. PREVIOUS STUDIES

2.1. Boronizing Methods

Boriding, or boronizing, is a thermo-chemical surface hardening process that can be applied to a wide variety of ferrous, nonferrous, and cermet materials.

The process involves heating well-cleaned material in the range of 700 °C to 1000 °C, preferably for 1 to 12 h, in contact with a boron solid powder (boronizing compound), paste, liquid, or gaseous medium.

Other developments in thermochemical boronizing include gas boronizing techniques such as plasma boronizing and fluidized bedboronizing. There is a current trend toward the use of multicomponent boronizing.

2.2. Characteristic Features of Boride Layers

The diffusion and subsequent absorption of boron atoms into the metallic lattice of the component surface form interstitial boron compounds results formation of boride layer during boronizing (A.G. von Matuschka, 1980).

The formed layer may consist of either a single-phase boride or a polyphase boride layer. The morphology, growth, and phase composition of the boride layer can be influenced by the alloying elements in the base material as represented in Figure 2.1 (R. Chatterjee and Fischer, 1981).

The microhardness of the borided layer depends strongly on the composition and structure of the boride layer and the composition of the base material as shown in Table 2.1 (Galibois et al, 1980).

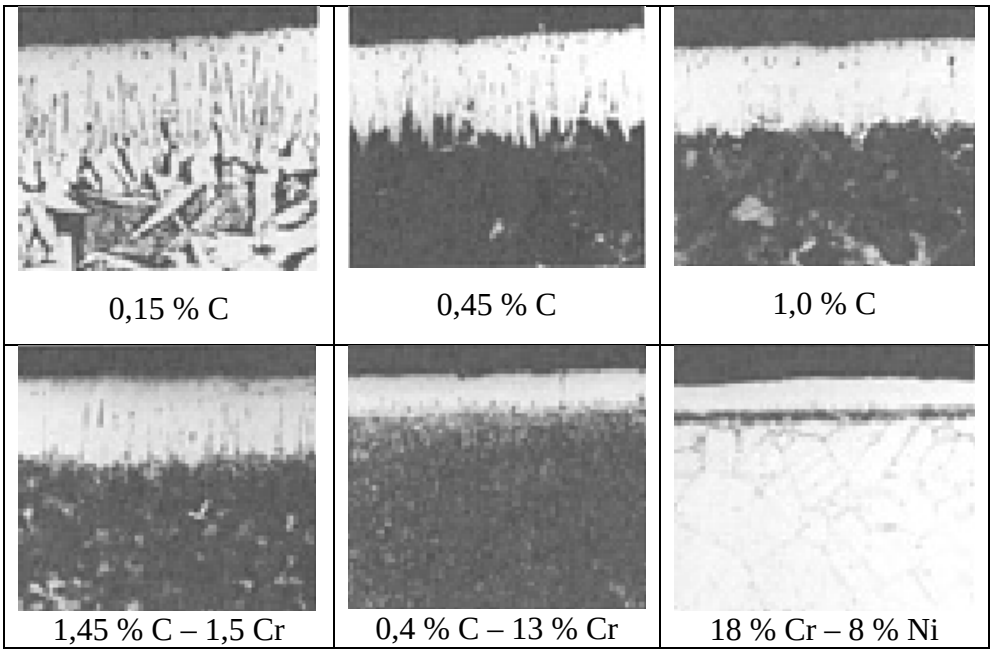

Figure 2.1. Effect of steel composition on the morphology and thickness of the boride layer (Asm Handbook, Vol.4, 2000)

Table 2.1. Melting point and microhardness of different boride formed during boronizing of different substrate materials (Asm Handbook, Vol.4, 2000)

Subsrate	Constiuent phases in boride layer	Microhardness of layers, HV or kg/mm^2	Melting point	
			°C	°F
Fe	FeB	1900-2100	1390	2535
	Fe_2B	1800-2000	…	…
Co	CoB	1850	…	…
	Co_2B	1500-1600	…	…
	Co_3B	700-800	…	…
Co-27,5Cr	CoB	2200 (100g)[a]	…	…
	Co_2B	~1550 (100g)[a]	…	…
	Co_3B?	700-800	…	…
Ni	Ni_4B_3	1600	…	…
	Ni_2B	1500	…	…
	Ni_3B	900	…	…
Inco 100	…	1700 (200g)[b]	…	…
Mo	Mo_2B	1660	2000	3630
	MoB_2	2330	~2100	~3810
	Mo_2B_5	2400-2700	2100	3810
W	W_2B_5	2600	2300	4170
Ti	TiB	2500	~1900	3450
	TiB_2	3370	2980	5395
Ti-6Al-4V	TiB		…	…
	TiB_2	3000 (100g)[a]	…	…
Nb	NbB_2	2200	3050	5520
	NbB_4		…	…
Ta	Ta_2B		3200-3500	5790-6330
	TaB2	2500	3200	5790
Hf	HfB2	2900	3250	5880
Zr	ZrB2	2250	3040	5500
a: 100 g load, b: 200 g load				

2.3. Advantages of Boronizing

Boride layers have a number of characteristic features with special advantages due to conventional casehardened layers.

One basic advantage is that boride layers have extremely high hardness values between 1450 HV and 5000 HV with high melting points of the constituent phases as demonstrated in Table 2.1.

The typical surface hardness values of boronized steels compared with other treatments and other hard materials are listed in Table 2.2. This clearly illustrates that the hardness of boride layers produced on carbon steels is much greater than that produced by any other conventional surface (hardening) treatments; it exceeds that of the hardened tool steel, hard chrome electroplate, and is equivalent to that of tungsten carbide (Asm Handbook, Vol.4, 2000).

Table 2.2. Typical surface hardness of borided steels compared with other treatments and hard materials (Asm Handbook, vol.4, 2000)

Material	Microhardness kg/mm2 or HV
Boride mild steel	1600
Borided AISI H13 die steel	1800
Borided AISI A2 steel	1900
Quenched steel	900
Hardened and tempered H13 die steel	540-600
Hardened and tempered A2 die steel	630-700
High-speed steel BM42	900-910
Nitrided steels	650-1700
Carburized low-alloy steels	650-950
Hard chromium plating	1000-1200
Cemented carbides, WC + Co	1160-1820 (30 kg)
Al2O3 + ZrO2 ceramic	1483 (30 kg)
Al2O3 + TiC + ZrO2 ceramic	1738 (30kg)
Sialon ceramic	1569 (30kg)
TiN	2000
TiC	3500
SiC	4000
B4C	5000
Diamond	>10.000

The combination of hard surface hardness and a low surface coefficient of friction of the boride layer also make significant contribution in combating the main wear mechanism: adhesion, tribooxidation abrazyon and surface fatigue (W.J.G. Fichtl; 1983, K.H. Habing and R.Chatterjee-Fische; 1981).

This fact has enabled the mold makers to substitute easier to machine steels for the base metal and to steel obtain wear resistance and and galling properties superior to those of the original material (D.J. Bak, 1981).

Figure 2.2 points out the effect of boronizing on abrasive wear resistance of borided C45 steel, titanium and tantalum as a function of number of revolutions (or stressing period) based on wear test.

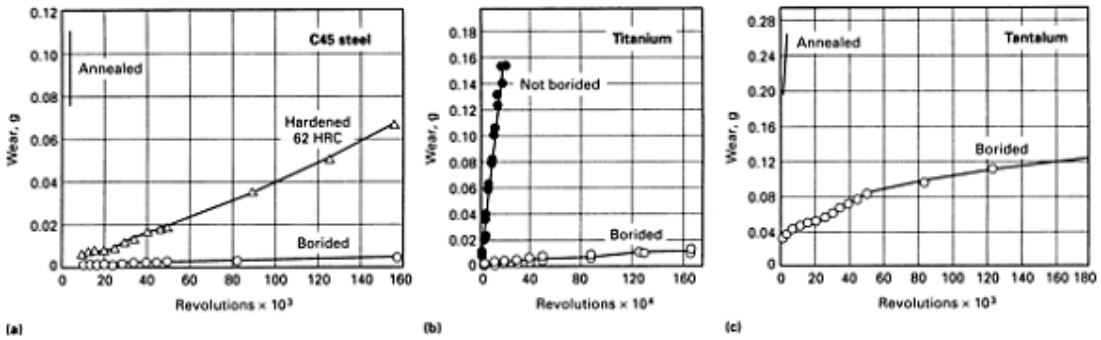

Figure 2.2. Effect of boronizing on the wear resistance a) 0.45 % C (C45) steel boronized 900 ºC b)Titanium boronized at 1000 ºC for 24h c) Tantalum boronized at 1000 ºC for 8h (Asm Handbook vol. 4, 2000)

Figure 2.3 shows the influence of steel composition on abrasive wear resistance.

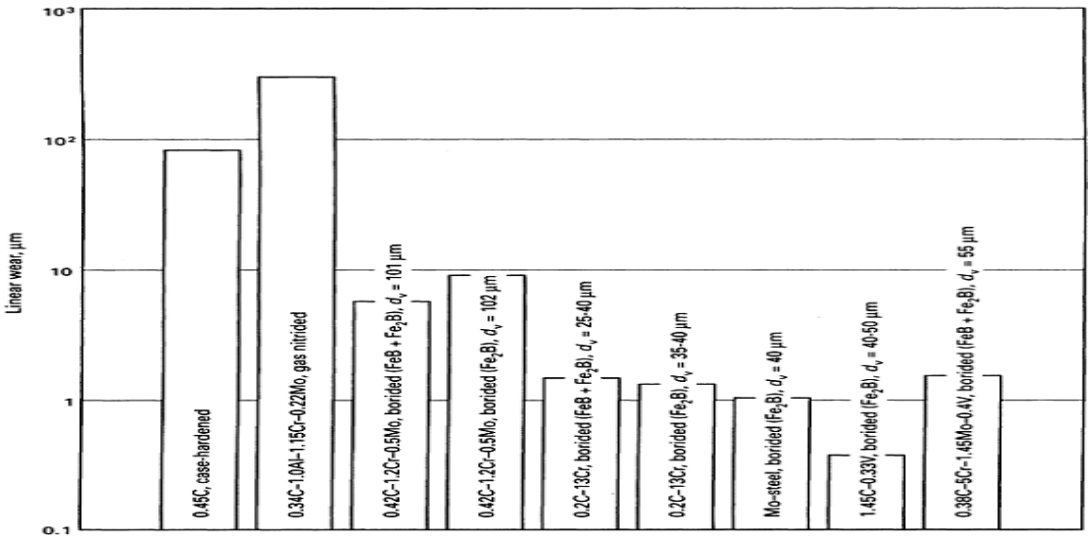

Figure 2.3. Effect of steel composition on wear resistance under abrasive wear. Test conditions: DP-U grinding tester, SiC paper 220, testing time 6 min. (Asm handbook, Vol.4, 2000)

Other advantages of boronizing include:

- Hardness of the boride layer can be retained at higher temperatures than, for example, that of nitrided cases.
- A wide variety of steels, including through hardenable steels, are compatible with the processes (Mater. Eng, 1970).
- Boronizing enhances the corrosion erosion resistance of ferrous materials in nonoxidizing dilute acids as indicated in Figure 2.4 and alkali media, is increasingly used to this advantage in many industrial applications (W.J.G. Fichtl).
- Borided surfaces have moderate oxidation resistance (up to 850 °C) and are quite resistant to attack by molten metals.
- Borided parts have an increased fatigue life and service performance under oxidizing and corrosive environments.

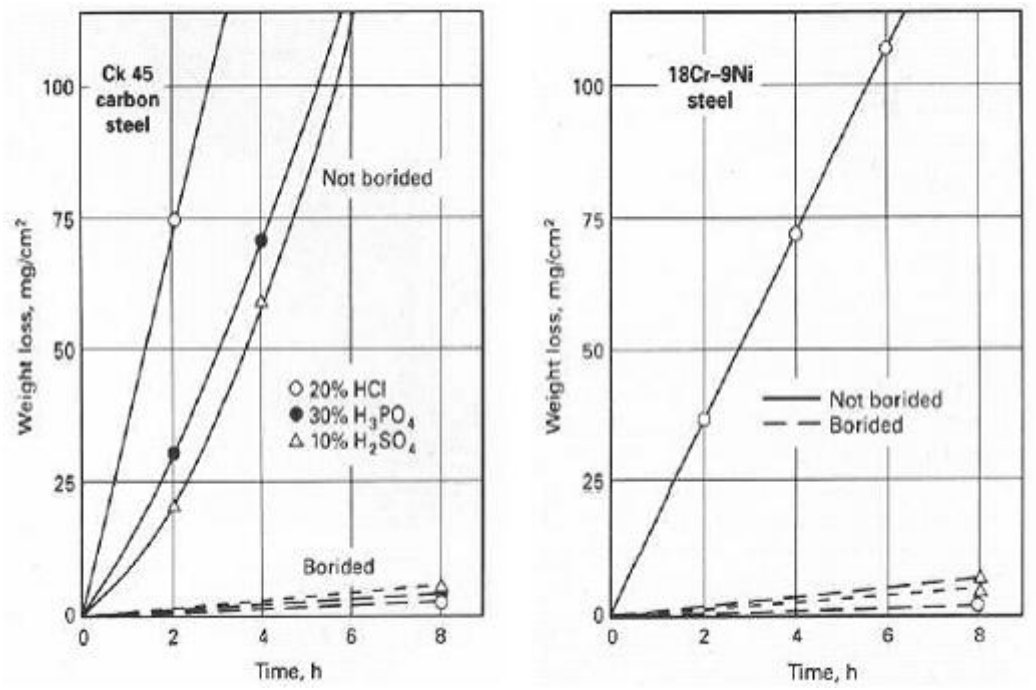

Figure 2.4. Corroding effect of mineral acids on boronized and nonboronized (a) 0.45% C (Ck 45) steel and (b) l8Cr-9Ni (X10CrNiTi18 9) steel at 56 °C (Asm handbook, Vol. 4, 2000)

2.4. Disadvantages of Boronizing

The techniques are inflexible and rather labor intensive, making the process less cost effective than other thermochemical surface hardening treatments such as gas carburizing and plasmanitriding.

Both gas carburizing and plasmanitriding have the advantage over boronizing because those two processes are flexible systems, offer reduced operating and maintenance costs, require shorter processing times, and are relatively easy to operate.

It is, therefore, suited to engineering components that need high hardness and outstanding wear and corrosion resistance of the boride layers, and/or where cheaper labor is available (P. Dearnly, T. Bell, 1985).

The growth (that is, the increase in volume) resulting from boronizing is 5 to 25% of the layer thickness (for example, 25 μm, or 1000 μin., layer would have a growth of 1.25 to 6.25 μm, or 50 to 250 μin.); its magnitude depends on the base material composition but remains consistent for a given combination of material and

treatment cycle. However, it can be predicted for a given part geometry and boronizing treatment.

For treatment of precision parts, where little stock removal is permitted, an allowance of 20 to 25% dimensional increase of the final boride layer thickness must be provided. Partial removal of the boride layer for closer tolerance requirements is made possible only by a subsequent diamond lapping because conventional grinding causes fracture of the layer. Thus, precise boronizing is mostly practiced for components with a large cross-sectional area (P. Dearnly, T. Bell,1985).

Boronizing of most steels provides a marginal increase, if any, in the bending fatigue endurance limit, although some improvement in the corrosion-fatigue strength has been noticed. In general, the rolling contact fatigue properties of boronized alloy steel parts are very poor compared to carburized and nitrided steels at high contact loads (2000 N). This is why boronizing treatments of gears are limited to those screw designs where transverse loading of gear teeth is minimized (P. Dearnly, T. Bell, 1985).

There is frequently a need to harden and temper the tool after boronizing (H.C. Child, 1981) which requires a vacuum or inert atmosphere to preserve the integrity of the boride layer.

2.5. Boride Layer on Ferrous Materials

Unlike carburizing treatment on ferrous materials, where there is a gradual decrease in composition from the carbon rich surface to the substrate, the boronizing of ferrous materials results in the formation of either a single-phase or double-phase layer of borides with definite compositions.

The single-phase boride layer consists of Fe2B, while the double-phase layer consists of an outer dark-etching phase of FeB and an inner bright-etching phase of Fe2B.

The formation of either a single or double phase depends on the availability of boron (R. Chatterjee-Fischer, 1977).

2.5.1. Characteristics of FeB and Fe_2B Layers

The formation of a single Fe2B phase (with a saw tooth morphology due to preferred diffusion direction) is more desirable than a double-phase layer with FeB.

The boron-rich FeB phase is considered undesirable, in part, because FeB is more brittle than the iron subboride Fe2B layer. Also, because FeB and Fe2B are formed under tensile and compressive residual stresses, respectively, crack formation is often observed at or in the neighborhood of the FeB/Fe_2B interface of a double-phase layer.

These cracks may lead to flaking and spalling when a mechanical strain is applied (Galibois et al, 1980) or even separation (Figure 2.5) when a component is undergoing a thermal and/or mechanical shock. Therefore, the boron-rich FeB phase should be avoided or minimized in the boride layer (Galibois et al, 1980).

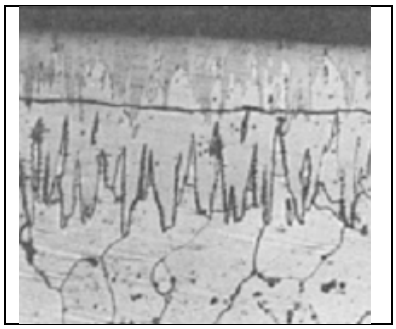

Figure 2.5. Separation of two-phase boride layer on a low-carbon (St 37) steel (boronized at 900 °C for 4 h) caused by grinding with a cutting-off disk. 200×, (Asm Handbook, Vol.4, 2000)

It has also been reported that the tribological properties depend on the microstructure of the boride layer. The dual-phase FeB-Fe2B layers are not inferior to those of monophase Fe2B layers, provided that the porous surface zone directly beneath the surface is removed (W. Liluental et al, 1983). Alternatively, a thinner layer is favored because of less development of brittle and porous surface-zone formation and flaking.

Typical properties of the FeB phase are:

- Microhardness of about 19 to 21 Gpa (2.7×10^6 to 3.0×10^6 psi).
- Modulus of elasticity of 590 Gpa (85×10^6 psi).
- Density of 6.75 g/cm^3.
- Thermal expansion coefficient of 23 ppm/°C between 200 and 600 °C (Ref 6 and17).
- Composition with 16.23 wt% boron.
- Orthorhombic crystal structure with 4 iron and 4 boron atoms per unit cell.
- Lattice parameters: a= 4.053 Å , b= 5.495 Å, and c =2.946 Å.

A single Fe2B phase can be obtained from a double FeB-Fe2B phase by a subsequent vacuum or salt bath treatment for several hours above 800 °C, which may be followed by oil quenching to increase substrate properties (P.A. Dearnly et al, 1986).

Typical properties of Fe2B are:

- Microhardness of about 18 to 20 Gpa (2.6×10^6 to 2.9×10^6psi).
- Modulus of elasticity of 285 to 295 Gpa (41×10^6 to 43×10^6psi).
- Thermal expansion coefficient of 7.65 ppm/°C and 9.2 ppm/°C in the range of 200 to 600 °C and 100 to 800 °C
- Density of 7.43 g/cm$^{3.}$
- Composition with 8.83 wt% boron.
- Body-centered tetragonal structure with 12 atoms per unit cell.
- Lattice parameters: a= 5.078 Å and c= 4.249 Å.

The solubility of boron in ferrite and austenite is very small (<0.008% at 900 °C) according to the Fe-B phase diagram (T.B. Massalski, 1986).

According to Brown (Brown et al. 1974) and Nicholson (M.E. Nicholson, 1954), the phase diagram exhibits an $\alpha/\gamma/Fe_2B$ peritectoid reaction at about

912°C, based on their findings of higher solubility of boron in ferrite than in austenite at the reaction temperature.

However, later work revealed a higher solubility of boron in austenite compared to that in ferrite, thereby suggesting the reaction is eutectoid in nature (T.b. Cameron and J.EMorral, 1986).

2.6. The Boronizing Process

The boronizing process consists of two types of reaction (R.Chatterjee-Fischer, 1989). The first reaction takes place between the boron yielding substance and the component surface. The nucleation rate of the particles at the surface depends on the boronizing time and temperature. This produces a thin, compact boride layer.

The subsequent second reaction is diffusion controlled, and the total thickness of the boride layer growth at a particular temperature can be calculated by the simple formula:

$$d = k\sqrt{t} \tag{2.1}$$

Where d is the boride layer thickness in centimeters; k is a constant, depending on the temperature; and t is the time in seconds at a given temperature.

The diffusivity of boron at 950 °C is $1.82 \times 10^{-8} cm^2/s$ for the boride layer and $1.53 \times 10^{-7} cm^2/s$ for the diffusion zone. As a result, the boron-containing diffusion zone extends more than 7 times the depth of boride layer thickness into the substrate

It has been proposed that a concentration gradient provides the driving force for diffusion-controlled boride layer growth (M.J Lu, 1983).

Diffusion case thicknesses range to approximately 0.13 mm for ferrous alloys, depending on alloy compositions and configurations. A lower case depth is required for the high-carbon and/or high-alloy tool steels, whereas higher case depths may be needed for the low or medium-carbon steels. When case depth is about 320 to 350 μm, subsequent heat treatment is not performed.

2.7. Boronizing of Ferrous Materials

With the exception of aluminum and silicon-bearing steels, industrial boronizing can be carried out on most ferrous materials such as structural steels; case-hardened, tempered, tool, and stainless steels; cast steels; Armco (commercially pure) iron; gray and ductile cast irons; and sintered iron and steel (W. Fitchl, 1972).

Because boronizing is conducted in the austenitic range, air-hardening steels can be simultaneously hardened and boronized. Water-hardening grades are not boronized because of the susceptibility of the boride layer to thermal shock.

Similarly, resulfurized and leaded steels should not be used because they have a tendency toward case spalling and case cracking.

Nitrided steels should not be used because of their sensitivity to cracking ("Boroalloy Process," Process Data Sheet 4, Lindberg Heat Treating Company)

2.7.1. Influence of Alloying Elements For Ferrous Materials

The mechanical properties of the boronized alloys depend on the composition and structure of the boride layers.

The characteristic saw tooth configuration of the boride layer is dominant with pure iron, unalloyed low-carbon steels, and low-alloy steels.

As the alloying element and/or carbon content of the substrate steel is increased, the development of a jagged boride/substrate interface is suppressed, and for high-alloy steels a smooth interface is formed (A.J. Ninham and I.M. Hutchings, 1989 and Fig.2.1).

Alloying elements mainly retard the boride layer thickness (or growth) caused by restricted diffusion of boron into the steel because of the formation of a diffusion barrier. Figure 2.6 shows the effect of alloying additions in steel on boride layer thickness (M.E. Blanter, 1955 and G.V. Samsonov, 1966).

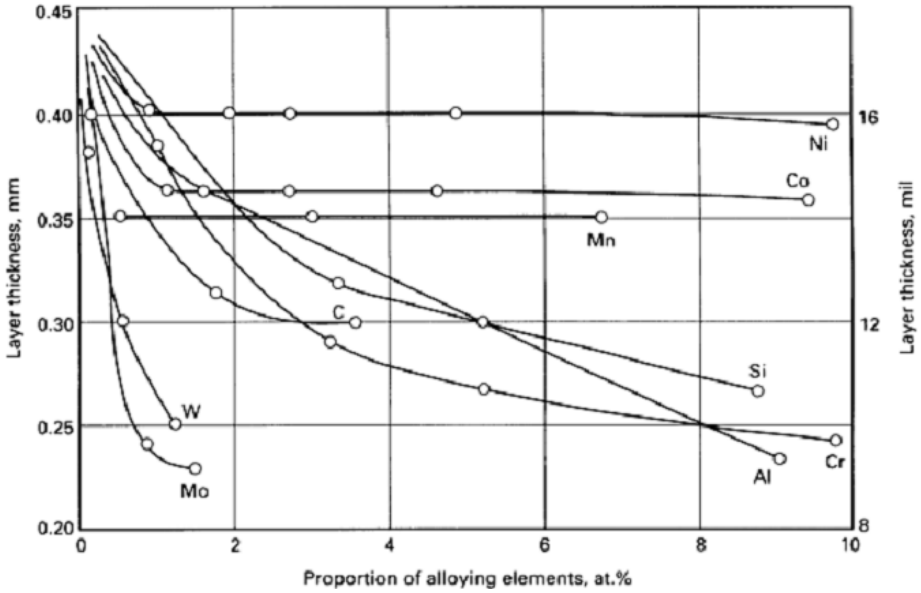

Figure 2.6. Effect of alloying elements in steel on boride layer thickness, (Asm Handbook, Vol.4, 2000)

Carbon does not dissolve significantly in the boride layer and does not diffuse through the boride layer. During boronizing carbon is driven (or diffused away) from the boride layer to the matrix and forms, together with boron, borocementite $Fe_3(B,C)$ [or more appropriately, $Fe_3(B_{0,67}C_{0,33})$ in the case of Fe-0.08% C steel] as a separate layer between Fe_2B and the matrix (J.J. Smit, 1984C.M. Brakman, 1988).

Like carbon, silicon and aluminum are not soluble in the boride layer, and these elements are pushed from the surface by boron and are displaced ahead of the boride layer into the substrate, forming iron silicoborides $FeSi_{0,4}B_{0,6}$ and Fe_5SiB_2 underneath the Fe_2B layer.

Steels containing high contents of these ferrite-forming elements should not be used for boronizing because they reduce the wear resistance of normal boride layer (A.G. von Matuschka, 1980); they produce a substantially softer ferrite zone beneath the boride layer than that of the core (H.C. Fielder and W.J. Hayes, 1970).

At higher surface pressure, this type of layer build up results in the so-called egg shell effect, that is, at greater thicknesses extremely hard and brittle

boride layer penetrates into the softer intermediate layer and is consequently destroyed (W.J.G. Fichtl, 1989).

A reduction in both the degree of inter locking tooth structure and of boride depth can occur with high nickel containing steels. Nickel has been found to concentrate below the boride layer; it enters the Fe_2B layer and in some instances promotes the precipitation of Ni_3B from the FeB layer (K.H. Habig, 1981).

It also segregates strongly to the surface from the underlying zone corresponding to the Fe_2B layer. This is quite pronounced in both Fe-14Ni and austenitic stainless steels. Consequently, gas boronizing of austenitic stainless steels appears to be a more appropriate treatment for producing a low-porosity, homogeneous, single-phase Fe_2B layer because of the lower boron activity of the gaseous mixture (P. Goeurits, 1982).

Chromium considerably modifies the structure and properties of iron borides. As the chromium content in the base material increases, progressive improvements in the following effects are observed:

- Formation of boron-rich reaction products.
- Decreasing in boride depth.
- Flattening or smoothening of the coating/substrate interface (M. Garbuccchio, 1985).

A reduction of boride thickness has also been noticed in ternary Fe-l2Cr-C steels with increasing carbon content (M. Garbuccchio,1985).

Manganese, tungsten, molybdenum, and vanadium also reduce the boride layer thickness and flatten out the tooth-shaped morphology in carbon steel.

The distribution of titanium, cobalt, sulfur, and phosphorus in the boride layer has not been well established.

2.8. Boronizing of Nonferrous Materials

Nonferrous materials such as nickel, cobalt, and molybdenum base alloys, as well as refractory metals and their alloys and cemented carbides can be boronized.

Copper cannot; therefore, it provides a good stopping-off material. Of special interest is the boronizing of nickel alloys and titanium and its alloys.

Usually, boronizing of nickel plate is done in gaseous BCl_3-H_2-Ar mixture in the temperature range of 500 to 1000 °C (S. Motojima et al, 1981), whereas Permalloy is pack boronized with 85% B_4C and 15% Na_2CO_3, or 95% B_4C and 5% $Na_2B_4O_7$ powder mixture at 1000 °C for 6 h in H_2 atmosphere.

Boronizing of titanium and its alloys is carried out preferably between 1000 and 1200 °C. Here pack boronizing in oxygen-free amorphous boron in combination with high-vacuum (0.0013 Pa, or 10^{-5}torr) and high-purity argon atmosphere or gas boronizing with H_2-BCl_3-Ar gas mixture is preferred.

The microhardness readings of boride layers formed on titanium and refractory metals are very high compared to those formed on cobalt and nickel (see Table 2.1).

The wear properties of sintered carbides can be increased by boronizing because of the acceptance of boron by soft cobalt and nickel binders (Lindberg heating treating company, “Boroalloy Process”).

Boride layers formed on tantalum, niobium, tungsten, molybdenum, and nickel do not have tooth-shaped morphology as with titanium.

When cemented carbides (such as WC-Co wire-drawing dies) are commercially pack boronized with a powder mixture containing 40% B_4C, 45% SiC, and 5% KBF_4, three distinct zones are found to be formed in the boride layer comprising the exterior (zone I), intermediate (zone II), and interior (zone III) regions as represented in Table 2.3.

Table 2.3 Three distinct zones formed in boronized cemented carbide materials (AsmHandbook, Vol.4, 2000)

Zone	Reference 38	Reference 7
I	CoB, W_2B_5, WC	CoB, WC
II	W_2CoB_2, WCoB, WC	Co_2B, WC
III	$W_2Co_2B_6$, WC, Co	Co_3B, WC

2.8.1 Effects of Alloying Elements For Nonferrous Materials

As in iron and steel, suitable alloying additions raise the hardness of the boride layer formed on these metals; this is presumably caused by the formation of solid-solution borides.

Additions of alloying elements in nickel, cobalt, and titanium retard the rate of boride layer growth, and in the case of multiphase layers, the proportion of boride layer with high boron content (for example, TiB_2 in titanium) increases.

The tooth-shaped morphologies in the cases of cobalt and titanium are also retarded with alloying addition, and the layers appear more uniform (R. Chatterjee et al, 1976).

2.9 Heat Treatment after Boronizing

Boronized parts can be quench hardened in air, oil, salt bath, or polymer quenchant and subsequently tempered. Heating to the hardening temperature should be carried out in an oxygen-free protective atmosphere or in a neutral salt bath (R.Chatterjee-Fischer, 1989).

2.10 Thermochemical Boronizing Techniques

Because extensive investigations have been carried out on boronizing of ferrous materials, the techniques described below focus mainly on the boronizing of ferrous materials.

2.10.1 Pack Boronizing

Pack boronizing (V.A. Volkov et al, 1975 and N. Komutsu et al, 1974) is the most widely used boronizing process because of its relative ease of handling, safety, and the possibility of changing the composition of the powder mix, the need for limited equipment, and the resultant economic savings (Matuschka, 1980).

The process involves packing the annealed, cleaned, smooth parts in a boronizing powder mixture contained in a 3 to 5 mm (0.1 to 0.2 in.) thick, heat-resistant steel box so that surfaces to be boronized are covered with an approximately 10 to 20 mm (0.4 to 0.8 in.) thick layer.

Many different boronizing compounds have been used for pack boronizing. They include solid boron yielding substances, diluents, and activators.

The common boron yielding substances are boron carbide (B_4C), ferroboron, and amorphous boron; the last two have greater boron potential, provide a thicker layer, and are more expensive than B_4C (N. Komutsu et al, 1974).

Silicon carbide (SiC) and alumina (Al_2O_3) serve as diluents, and they do not take part in the reaction. However, SIC controls the amount of boron and prevents packing of the boronizing agent.

$NaBF_4$, KBF_4, $(NH_4)_3BF_4$, NH_4Cl, Na_2CO_3, BaF_2, and $Na_2B_4O_7$ are the boronizing activators.There are special proprietary brands of boronizing compounds, such as different grades of Ekabor, available on the market that can be used with confidence. Typical compositions of commercial solid boronizing powder mixtures are:

- 5% B_4C, 90% SiC, 5% KBF_4
- 50% B_4C, 45% SiC, 5% KBF_4
- 85% B_4C, 15% Na_2CO_3
- 95% B_4C, 5% Na_2CO_3
- Amorphous boron (containing95 to 97% B)
- 95% amorphous boron, 5% KBF4

The parts conforming to the shape of the container are packed (Figure 2.7), covered with a lid, which rests inside the container and is weighted with an iron slug or stone to ensure an even trickling of the boronizing agent during the boronizing treatment. It is then heated to the boronizing temperature in an electrically heated box or pit furnace with open or covered heating coils or a muffle furnace for a specified time. The container should not exceed 60% of the furnace chamber volume.

In principle, boronizing should be accomplished in such a way that high internal stresses are relieved, which in turn, eliminates cracks or spalling. With the packing process, the powder may be reused by blending with 20 to 50 wt% of fresh powder mixture. In this case, the powder should be discarded after 5 or 66 cycles (AsmHandbook, vol.4, 2000).

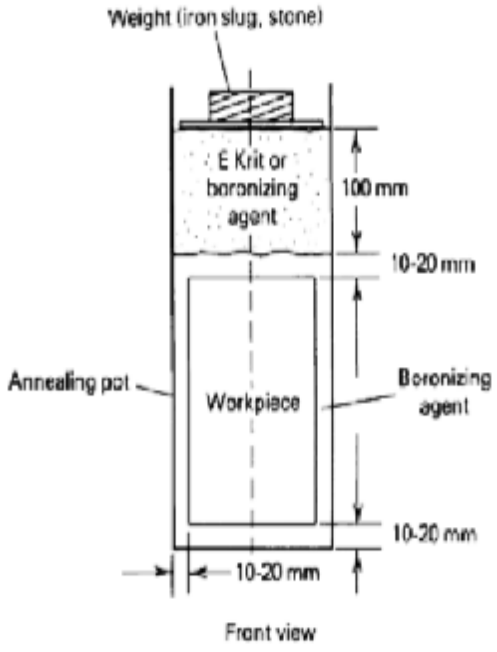

Figure 2.7. Diagram of the packing of a single geometrical part in a pack boronizing box (AsmHandbook, vol.4, 2000)

2.10.2 Case Depth

The thickness of the boride layer depends on the substrate material being processed, boron potential of the boronizing compound (Fig. 2.8), boronizing temperature, and time (Fig.2.9).

In ferrous materials, the heating rate especially between 700 °C and the boronizing temperature (800 to 1000 °C) should be high in order to minimize the formation of FeB (R. Chatterjee, 1989).

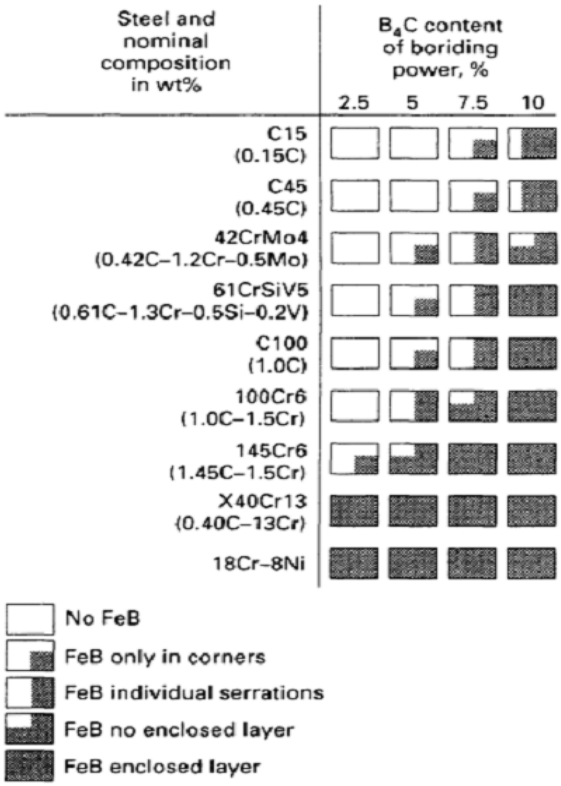

Figure 2.8. Diagram showing the influence of the B4C content of the boronizing powder on the proportion of FeB phase in the boride layer of various steels borided with pack powder at 900°C for 5 h (AsmHandbook, vol.4, 2000)

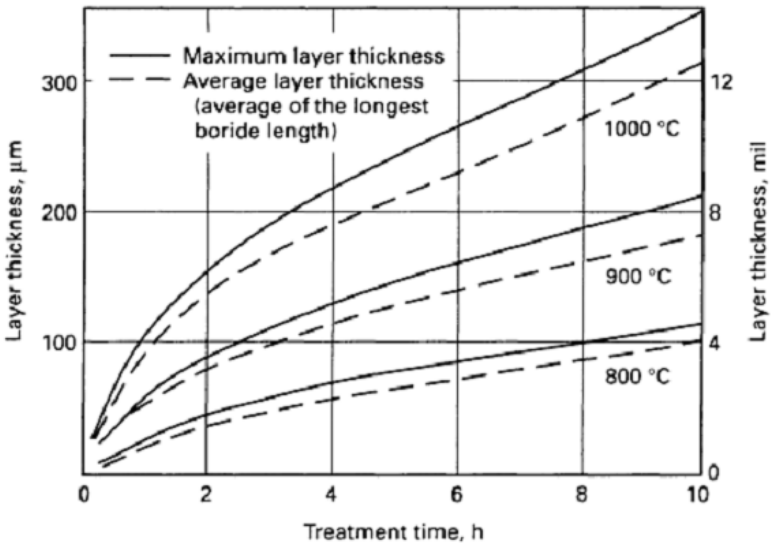

Figure 2.9. Effect of pack boronizing temperature and time on the boride layer thickness in a low-carbon (Ck 45) steel (AsmHandbook, vol.4, 2000)

It is usual practice to match the case depth with the intended application and base material.

As a rule, thin layers (for example, 15 to 20 μm) are used for protection against adhesive wear (such as chipless shaping and metal-stamping dies and tools), whereas thick layers are recommended to combat erosive wear (for example, extrusion tooling for plastics with abrasive fillers and pressing tools for the ceramic industry).

The commonly produced case depths are 0.05 to 0.25 mm (0.002 to 0.01 in.) for low-alloy and low-carbon steels and 0.025 to 0.076 mm (0.001 to 0.003 in.) for high-alloy steels.

However, case depths >0.089 mm (>0.0035 in.) are uneconomical for highly alloyed materials such as stainless steels and some tool steels (Lindberg heating treating company, “Boroalloy Process”).

2.10.3. Paste Boronizing

Paste boronizing is used commercially when pack boronizing is difficult, more expensive, or time consuming (Goeuriot et al, 1981).

In this process, a paste of 45% B4C (grain size 200 to 240 μm) and 55% cryolite (Na3AlF6, flux additive) or conventional boronizing powder mixture (B4C-SiC-KBF4) in a good binding agent (such as nitrocellulose dissolved in butyl acetate, aqueous solution of methyl cellulose, or hydrolyzed ethyl silicate) is repeatedly applied (that is, brushed or sprayed) at intervals over the entire or selected portion of parts until, after drying, a layer about 1 to 2 mm (0.04 to 0.08 in.) thick is obtained.

Subsequently, the ferrous materials are heated (900 °C for 4 h) inductively, resistively, or in a conventional furnace to 800 to 1000 °C for 5 h.

In this process, a protective atmosphere (for example, argon, cracked NH3, or N2) is necessary.

A layer in excess of 50 μm thickness may be obtained after inductively or resistively heating to 1000 °C for 20 min (Figure 2.10).

This process is of special interest for large components or for those requiring partial (or selective) boronizing.

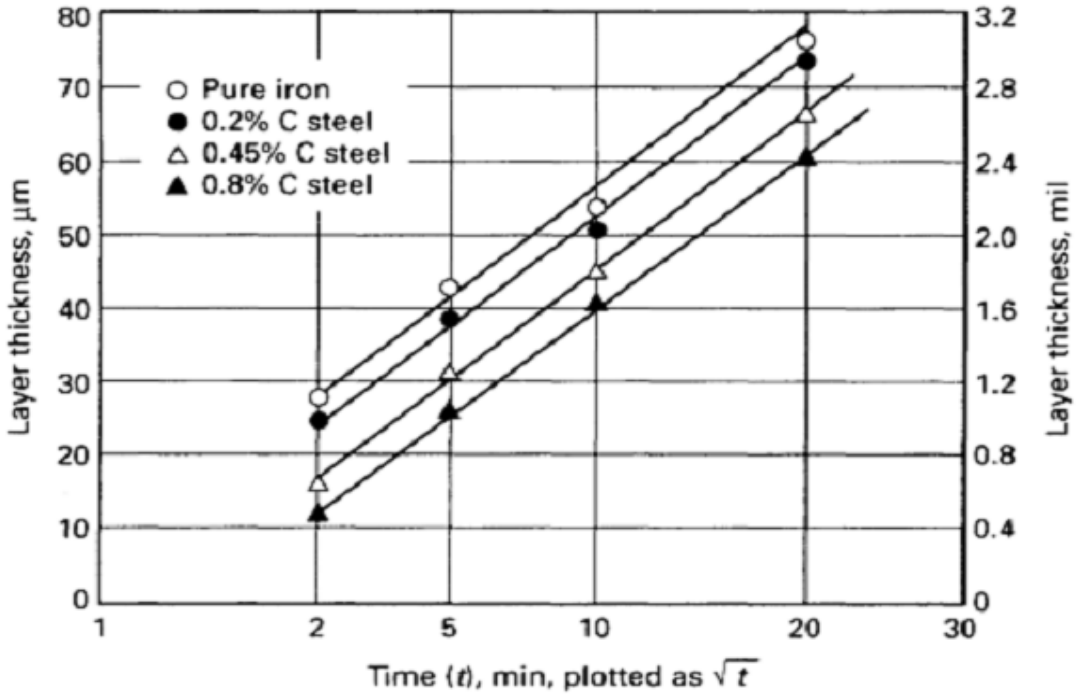

Figure 2.10. A linear relationship between boride layer thickness and time for iron and steel boronized withB4C-Na2B4O7-Na3AlF6based paste at 1000 °C

2.10.4. Liquid Boronizing

Liquid boronizing is grouped into electroless and electrolytic salt bath processes. These processes have several disadvantages:

- Removal of excess salt and unreacted boron is essential after the treatment; this step may prove to be expensive and time consuming.
- To achieve boronizing reproducibility, bath viscosity is not allowed to increase. This is done by recharging with salt, which involves high maintenance costs.
- In some situations protection from corrosive fumes may be required.

2.10.4.1. Electroless Salt Bath Boronizing

Electroless salt bath boronizing of ferrous materials is carried out in a borax-based melt at about 900 to 950 °C, to which about 30 wt% B_4C is added (Lyakhovich et al, 1971).

The boronizing action can be further improved by replacing up to 20 wt% B_4C with ferro aluminum because it is a more effective reductant. However, superior results have been found by using a salt bath mixture containing 55% borax, 40 to 50% ferroboron, and 4 to 5% ferro aluminum (Hosokawa et al, 1972)

It has also been shown that 75:25 KBF_4-KF salt bath can be used at temperature below 670 °C for boronizing nickel alloys, and at higher temperatures for ferrous alloys, to develop the desired boride layer thickness.

2.10.4.2. Electrolytic Salt Bath Boronizing

In this process, the ferrous part acting as the cathode and a graphite anode are immersed in the electrolytic molten borax at 940 °C for 4 h using a current density of about 0.15 A/cm^2

Then parts are air cooled. In general, the parts are rotated during the treatment to obtain a uniform layer.

A high current density produces a thin coating on low-alloy steels in a short time. For high-alloy steels of greater thickness, lower current densities are required for a longer time

In the fused state tetraborate decomposes into boric acid and nascent oxygen.

$B_4O_7 + 2e = 2B_2O_3 + O$

$6\ Na + B_2O_3 = 3\ Na_2O + 2B$

Simultaneously, sodium ions, after being neutralized in the vicinity of cathode, react with boric acid to liberate boron.

In this manner, a high boronizing potential is established near the cathode region. Other satisfactory electrolytic salt bath compositions include:

- KBF_4-LiF-NaF-KF mixture for parts to be treated at 600 to 900 °C
- 20KF-30NaF-50LiF-0.7BF_2 mixture (by mole %) at 800 to 900 °C in 90N_2-10H_2 atmosphere.
- 9:1 (KF-LiF)-KBF_4 mixture under argon atmosphere
- KBF_4-NaCl mixture at 650 °C
- 90(30LiF+ 70KF)-10KBF_4 mixture at 700 to 850 °C
- 80$Na_2B_4O_7$-20NaCl at 800 to 900 °C

Gas boronizing may be accomplished with:

- Diborane (B_2H_6)-H_2 mixture.
- Boron halide-H_2/or (75:25 N_2-H_2) gas mixture.
- Organic boron compounds such as $(CH_3)_3B$ and $(C_2H_5)_3B$.

Boronizing with B2H6-H2 mixture is not commercially viable due to the high toxic and explosive nature of diborane

When organic boron compounds are used, carbide and boride layers form simultaneously. Because BBr3 is expensive and is difficult to handle (with violent reactions with water), and because BF3 requires high reduction temperature (due to its greater stability) and produces HF fumes, BCl_3 remains the attractive choice for gas boronizing.

When parts are gas boronized in a dilute (1:15) BCl3-H2 gas mixture at a temperature of 700 to 950 °C and a pressure up to 67 kPa (0.67 bar), a boride layer 120 to 150 μm thick is reported to be produced at 920 °C in 2 h

Recent work has suggested the use of 75:25N2-H2 gas mixture instead of H2 gas for its better performance because of the production of boride layers with minimum FeB content. The latter phase can be eliminated during the subsequent diffusion treatment before hardening. This process can be applied to titanium and its alloys as well.

2.10.5. Plasma Boronizing

Both mixtures of B2H6-H2 and BCl3-H2-Ar may be used successfully in plasma boronizing (Filep et al, 1980)

However, the former gas mixture can be applied to produce boride layer on various steels at relatively low temperatures such as 600 °C, which is impossible with a pack or liquid boronizing process (Casadesus et al, 1979).

It has been claimed that plasma boronizing in a mixture of BCl3-H2-Ar gases shows good features such as better control of BCl3 concentration, reduction of the discharge voltage, and higher microhardness of the boride films (Raveh et al, 1983).

Figure 2.11 shows a schematic layout of a plasma boronizing facility.

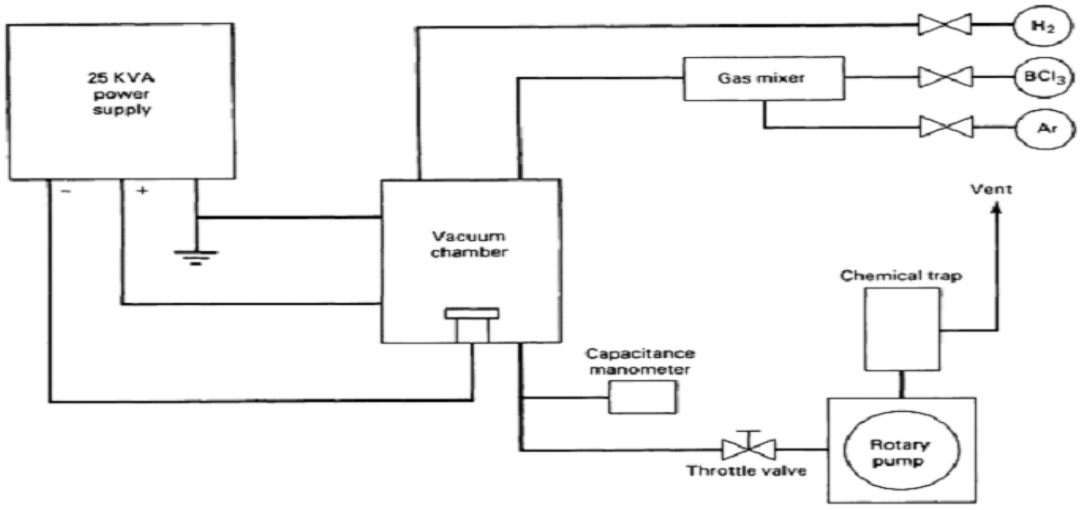

Figure 2.11. Layout of plasma boronizing facility

The dual-phase layer is characterized by visible porosity, occasionally associated with a black boron deposit. This porosity, however, can be minimized by increasing the BCl3 concentration.

Boride layers up to 200 μm in thickness can be produced in steels after 6 h treatment at a temperature of 700 to 850 °C and a pressure of 270 to 800 Pa (2 to 6 torr) (Wierzchon et al, 1980).

Advantages of this process are:

- Control of composition and depth of the boronized layer.
- Increased boron potential compared to conventional pack boronizing.
- Finer plasma-treated boride layers.
- Reduction in temperature and duration of treatment.
- Elimination of high-temperature furnaces and their accessories.
- Savings in energy and gas consumption.

The only disadvantage of the process is the extreme toxicity of the atmosphere employed. As a result, this process has not gained commercial acceptance. To avoid the above shortcoming, boronizing from paste (containing a mixture of 60% amorphous boron and 40% liquid borax) in a glow discharge at the

impregnating temperature has been recently developed, which is found to greatly increase the formation of the surface boride layer (Isakov et al, 1987).

2.11. Application of Pack Boronizing

Uslu et al (2007), performed boronizing method at 800, 875, and 950 Celsius degrees for 2, 4, 6, and 8 hours using Ekabor 2 powders on AISI 1040 and AISI P20 steel. They found borides formed on the surface of both steels have columnar morphology. In addition they showed that the micro hardness of borides formed on the surface of AISI P20 is higher than AISI 1040 steel and the fracture toughness of borides formed on the surface of AISI 1040 carbon steel is higher than AISI P20 mold steel.

Ozbek et al. (2004), investigated some properties of borides formed on AISI 440C stainless-steel. Boronizing was carried out in a solid medium consist of Ekabor2 powder at a temperature of 950 ºC for 2-8 hours. As a result of the microstructure analysis, the presence of borides (FeB, Fe2B, CrB, MnB, etc.) was identified X-ray diffraction and Vickers hardness values of borides formed on the surface of AISI 440C substrate was over 2500 HVN.

Selçuk et al. (2003), investigated participation of boronizing, carburizing and carbonitriding processes to mechanical properties of plain carbon steel and alloy steel. They found that boronizing is the most effective thermochemical treatment for all ferro materials. But, the boronized layers are shallow and brittle. Therefore, boronizing provides excellent wear resistance under only light loads. This treatment can be applied to all steel but particularly to low alloyed steels

Tabur et al. (2009), examined abrasive wear behavior of the samples which were applied to solid boronizing at different temperatures and treatment of AISI 8620 steel which includes plain carbon and alloy elements. Abrasive test were conducted using pin on disc test apparatus which were 80 and 120 mesh aluminum oxide (Al2O3) abrasive papers and the samples were subjected to abrasion under 10, 20 and 30 N loads. They found that boronized steels exhibited an improvement in

abrasive wear resistance reaching up to 500%. In conclusion max hardness value was obtained at 950 °C and 6 hours.

Kayali et al. (2001), researched boro-tempered ductile iron on properties of adhesion and wear. Firstly, the samples were boronized by using pack process at 900 °C for 1, 3, and 5 h and then, secondly tempered at 250, 300, 350, and 400 °C for 1 h. Wear tests indicated that boro-tempering heat treatment increased wear resistance of ductile iron. In addition, it was found that while wear rate of boro-tempered samples decreased with increasing boronizing time, there is no significant effect of tempering temperature on wear rate.

Yılmaz and Varol (2010), searched the effect of surface hardening treatments on the mechanical properties of iron based P/M specimens which consists of 3% Cu+ 0.2% C +balance Fe%. They found that surface hardness values such as 1800–2500 HV were achieved after boronizing, the difference between the matrix materials with a hardness of 200 HV was quite high.

The effects of conventional heat treatment and boronizing on SAE 1010 and SAE 1040 structural steels, D2 tool steel, and 304 stainless steel were investigated by Atıket al. (2003), The best wear strengths were obtained in boronizing 8 hours at 900°C for SAE 1010 and SAE 1040 steels, 4 hours at 900°C for D2 steel and 6 hours at 900% for 304 steel. In corrosive environments in which 10% H2SO4 was used, the best corrosion resistance was obtained from8 hours boronizing at 900°C for SAE 1010, and SAE 1040, D2, and 304 steels. Hardness value results show that there is not a linear relationship between hardness values and wear and that high values of hardness affect the wear negatively in D2 and 304 steels. The microhardness values, corrosion resistances and wear strengths of boronized specimens were found to be higher than for other specimens. In this tribological system, it has been found that wear strengths were not directly related to the layer thicknesses, hardnesses and corrosion resistances. This confirms that wear strength is a system property. Their experimental study showed that boronizing had much better wear and corrosion resistance than other applied surface hardening methods.

Sen U and Sen S. (2003) investigated the fracture toughness of boride layers of two boronized cold work tool steels. Boronizing was carried out in a salt bath

consisting of borax, boric acid, ferro-silicon and aluminum. Boronizing was performed at 850 and 950 °C for 2 to 7h. Increasing of boronizing time and temperature leads to reduction of fracture toughness of borides. Metallographic examination showed that boride layer formed on cold work tool steels was compact and smooth

Pack boronizing of pure vanadium was performed by Tarakci et al. (2010) at 1100 °C for 4, 8, 12 and 16 h under a controlled atmosphere. The metallographic studies revealed that a single boride layer with dense, compact and relatively smooth morphology was formed on the surface of pure vanadium. The microhardness of the boride layer was approximately 3700 HV for all boronizing times. Thickness of the boride layer increased almost parabolically from about 23 to 50 μm with boronizing time. Surface roughness of the coating was relatively increased from approximately 0.58 to 2.25μm by boronizing duration.

Tsipaset al. (1999) studied the chemical properties of boride layers in aggressive environments that include dilute HCI. H3PO4, H2SO4, and HNO3, acid solutions and vapors of molten Al alloy and Zn metals in various temperature ranges. Results indicated that with the exception of HNO3acid, the presence of boride layers on Fe-alloys, greatly improved their corrosion resistance. Boride layers showed extreme resistance to these acids at temperatures between room temperatures and boiling points and also when exposed to the vapors of these acids at 96 °C

Smirnyagina et al. (2002) stated that B and B4C are more suitable boronizing agents than B2O3.

Ribeiro et al. (2007) researched the friction and wear characteristics of boronized tantalum against bearing steel E52100 under dry and simulated body fluid (SBF) conditions. They determined wear mechanisms and friction of the coating depended on the chemical environment and nature of debris, respectively. Their study showed that diffusion boronizing renders the metal coating much harder than the pure metal, but the coating is prone to cracking due to greater brittleness of the surface. When in contact with simulated body fluid, under tribological conditions, chemical reactions around the grains cause.

Ulutan et al. (2010) evaluated the tribological properties of boride layers on the surface of AISI 4140 steel, formed using the pack-boronizing method via Commercial EKabor 2 and following results were obtained:

- The boride layers formed at the surfaces of the AISI 4140 exhibit saw-tooth structures and the layer thickness increases with both boronizing time and temperature.
- The microhardness values of the boride layers varied between 1200 and 1750 HV0.05.
- Abrasive wear resistance of the boronized layers was approximately 3–4 times greater than that of the untreated samples. The best wear resistance was obtained for the sample boronized for 6 h at 900 °C.
- Coefficient of friction values for the steel specimens that featured boride layers were lower than the coefficient of friction values for untreated steel samples. The sample boronized at 950°C for 6 h exhibited the lowest COF, at a value of about 0.16. However, in situations where adhesive wear is important, but economical factors must be considered, good COF results can be obtained by boronizing for just four hours, at 1000 °C

Sen et al. (2006) investigated the wear behaviour of boronized and short-duration oxidized AISI 4140 steel. Boronizing was carried out in a slurry salt bath consisting of borax, boric acid and ferro silicon. The hardness of borides formed on the surface of steel substrate and unboronized steel substrate were 1446–1690 HV0,1 and 280 HV0,1 respectively. The highest wear rates were observed on disc slide against the base steel, whilst the lowest wear rates occurred during sliding against the boronized and short-duration oxidized steel surfaces. It was observed that the friction coefficient of unboronized (hardened + tempered) and boronized steels ranged from 0.50 to 0.60, but after short-duration oxidizing, the friction coefficient of boronized steel was dropped to 0.12

Study of Lubas was to determine the influence of technologically produced boron surface layers on the friction parameters in the sliding pairs under the

conditions of mixed friction. It was found that Boron-hardening reduced the friction coefficient during the start-up of the frictional pair (LUBAS, J., 2009

SUH et al. (2003) investigated the improvement of mechanical properties as a result of boronizing, according to the variation of heating conditions and materials. Boronizing was performed using four different types of steel for 2h, 3 h and 5h at 900 °C. Results showed that the depth of the boride layer is effected by the boronizing time and is deeper with longer boronizing time. The reheating of a boronized specimen produces a deeper boride layer. Surface hardness after boronizing, 1700~2100 HV is increased 8-10 times compared with before boronizing. This is because Fe and B form on solid solution there by making the crystal phase of the compound metals, FeB or Fe2B, on the specimen surface. When comparing a boronized specimen with a non-boronized one, its tensile strength is somewhat decreased, yet its ductility is increased. In the case of a reheated boronized specimen, its tensile strength is slightly decreased due to the influence of reheating, yet its ductility is greatly

2.12. Corrosion

The significant technical challenges and the high cost directly related to corrosion provide strong incentives for engineers and other technical personnel to develop a firm grasp on the fundamental bases of corrosion. Understanding the fundamentals of corrosion is necessary not only for identifying corrosion mechanisms, but also for preventing corrosion by appropriate corrosion protection means and for predicting the corrosion behavior of metallic materials in service conditions. Understanding the mechanisms of corrosion is the key to the development of a knowledge-based design of corrosion resistant alloys and to the prediction of the long-term behavior of metallic materials in corrosive environments.

Two major areas are usually distinguished in the corrosion of metals and alloys. The first area is where the metal or alloy is exposed to a liquid electrolyte, usually water, and thus typically called aqueous corrosion. The second area is where corrosion takes place in a gaseous environment, often called oxidation, high-

temperature oxidation, or high-temperature corrosion, and called gaseous corrosion here. These two areas have been referred to as wet corrosion and dry corrosion. This distinction finds its origin in some fundamental differences in the mechanisms, in particular the electrochemical nature of reactions occurring in aqueous solution, as compared to the formation of thick oxide layers in air or other oxidizing atmospheres, at high temperature with fast transport processes by solidstate diffusion through a growing oxide. The separation between the two areas, however, should not be over emphasized, because there are also similarities and analogies.

2.12.1. Electrolytes

A good electrolyte for ECM must have high electrical conductivity, high specific heat, good chemical and electrochemical stability, controllable passivating effect, low viscosity, and low toxicity and corrosivity (Ref 2,12). Electrolyte in the IEG conducts current between anode and cathode, removes reaction products, and dissipates heat produced during the process. The electrolytes perform better when the crystal structure of the workpiece is fine grained, and its constituent dissolve at uniform rate. Electrolytes used in ECM are classified in three categories: neutral salt, alkaline, and acidic. Each type has its own merits. Sludging electrolytes produce hydroxide sludges that must be removed before recycling.

Sodium chloride (NaCl) solutions are the most commonly used electrolytes in ECM. During ECM, water is depleted, producing H_2 gas and hydroxide which are insoluble in water. NaCl electrolyte is corrosive in nature and produces large amounts of sludge. The ratio of the amount of sludge formed to the amount of metal dissolved ranges between 6 and 8 for NaCl electrolyte.

There is no universal electrolyte that can be employed for every type of metal and alloy. Table 2.4 recommends some electrolytes for a limited range of metals and alloys. Under certain circumstances, mixtures of electrolytes, such as $NaNO_3$ and NaCl or NaCl and HCl, are used. For instance,

NaNO3 is passivating and more expensive, but gives smoother surfaces in certain cases.

Table 2.4. Electrolytes for the electrochemical machining of metals

Workpiece metal	Electrolyte			Removal rate	
	Major constituent	Concentration (max)			
		kg/L of H_2O	lb/gal of H_2O	$mm^3 \times 10^3$/min per 1000 A	$in.^3$/min per 1000 A
Steel; iron- nickel-, and cobalt-base alloys	NaCl or KCl	0.30	2.5	2.1	0.13
	$NaNO_3$	0.60	5	2.1	0.13
Steel; hardened tool steel	$NaClO_3$	0.78	6.5	2.0	0.12
Gray iron	NaCl	0.30	2.5	2.0[a][b]	0.12[a][b]
	$NaNO_3$	0.60	5	2.0[a][b]	0.12[a][b]
White cast iron	$NaNO_3$	0.60	5	1.6[c]	0.10[c]
Aluminum and aluminum alloys[d]	$NaNO_3$	0.60	5	2.1	0.13
	NaCl or KCl	0.30	2.5	2.1	0.13
Titanium alloys	NaCl or KCl[e]	0.12	1	1.6	0.10
Tungsten	NaOH[f]	0.18[g]	1.5[g]	1.0	0.06
Molybdenum	NaOH[h]	0.18	1.5	1.0	0.06
	NaCl or KCl	0.30	2.5	1.0	0.06
Copper and copper alloys[d]	NaCl or KCl	0.30	2.5	4.4	0.27
	$NaNO_3$	0.60	5	3.3	0.20
Zirconium	NaCl or KCl	0.30	2.5	2.1	0.13

(a) Feed rates limited by graphite particle size.

(b) Maximum; can vary widely.

(c) Rough surface finish.

(d) NaNO3 electrolyte provides better surface finish.

(e) Voltage must be greater than.

(f) NaOH used up in process and must be replenished.

(g) Minimum of 9 kg/L (0.75 lb/gal.)

(h) pH of electrolyte decreases with use; maintain pH by adding NaOH or KOH Ref

Tavakoli H. and Khoie S.M.M. (2010) were investigated the corrosion resistance of three special steels improved by thermo-reactive diffusion (TRD). They prepared samples from the test materials which were treated at graphite crucible bath where borax, boric acid and ferro-silicon were mixed. The coating process was done at 1220K for 6 h. The corrosion resistance of the boronized samples was evaluated by the Tafel polarisation and electrochemical impedance spectroscopy (EIS).

This study concluded that the results of electrochemical impedance spectroscopy technique and Tafel polarisation measurement were in reasonably good agreement.

Atık E. et al. (2002) investigated the effects of conventional heat treatment and boronizing on SAE 1010 and SAE 1040 structural steels, D2 tool steel, and 304 stainless steel. They examined the layer thicknesses, corrosion and wear strength by applying carburisation, nitriding, transformation hardening and boronizing to the specimens. They concluded the followings;

The best wear strengths were obtained in boronizing 8 hours at 900°C for SAE 1010 and SAE 1040 steels. 4 hours at 900°C for D2 steel and 6 hours at 900% for 304 steels.

By using 10% H_2SO_4 for obtaining corrosive environment, the best corrosion resistance was obtained from 8 hours boronizing at 900°C for SAE 1010, and SAE 1040, D2, and 304 steels.

The experimental study showed that boronizing had much better wear and corrosion resistance than other applied surface hardening methods.

3. MATERIAL AND METHOD

3.1. Material

In this study, the effects of boronizing processes paramaters on wear and corrosion resistance of AISI 1050 steel was investigated. AISI 1050 steel is widely used in different areas of machine constructions such as vehicle, engine, machine and machine component design and die sets. The chemical composition of material used in the experiments was given in Table 3.1.

Table 3.1. Chemical composition of 1050 steel (Kalite Metalurji Corp., 2014)

C %	Si %	Mn %	Pmax %	Smax %
0.42-0.50	0.15-0.35	0.50-0.80	0.045	0.045

Specimens whose lengths and diameters are 1000 mm and 12 mm respectively, are supplied from market for boronizing treatment. Turning machine was used to increase surface quality of the specimens. Since the specimen is slender, the specimen is cut to three identical pieces by chainsaw to prevent deflection in turning machine. Diameters of the specimens decreased to 11 mm in turning machine and their surface quality were increased using abrassive papers with 220, 100, 80 mesh sizes respectiveley. After these machining processes, six parts with 330 mm length and 11 mm diameter, were prepared. Prepared parts were then cut to different sizes for the following processes and tests.

Since the working ranges of the available wear resistance test machine in labaratory, is between 25 and 35 mm, specimen lengths are cut to 30 mm for wear resistance test.

10 mm length of specimens were prepared for hardness test and optical microscope. Specimen lengths have been kept small to increase sensivity in measurements of the hardness test machine. Therefore rigidity between the specimen and table have been increased during the hardness measurement.

15 mm length of specimens were prepared corrosion resistance test. They might be cut longer or shorter. But ideal length were 15 mm for our measurements due to testing of only one surface of the specimens.

All cutting processes were performed by using abrasive cutting machine, shown in Figure 3.1 available in the laboratory. Also chips that were formed after cutting process, were removed by grinding and polishing Machine which was shown in Figure 3.2 and surface quality of the specimen was increased.

Figure 3.1. Abrasive Cutting Machine

Figure 3.2. Grinding and Polishing Machine

3.1.1. Boron Powder

Pack borozing method with Ekabor 2 powder was used for boronizing speciements at different conditions .

Pack boronizing mixtures used in the experiments comprise 5% B4C as the source, 5% KBF4 as activator and 90% SiC as the diluting agent.

Many boron powders are available for pack boronizing. Boron agents that are commonly used, are given in Table 3.2.

Table 3.2. Boron agents that are commonly used (www.bortec.de)

Boronizing Agent	**Grain Size (µm)**	**Comments**
Ekabor1	< 150	Highest quality surface layer;tends to bond together
Ekabor2	< 1000	exellent surface layer; simple unpacking of the parts after treatment
Ekabor3	> 1000, 2000<	very good surface layer; flowability of the powder still good after treatment.
EkaborHM	< 150	For hard metal, small bore sizes and thick boride layers; very good surface layers
Ekabor-Paste	< 100	Applicable universally; immersion,brushing,spraying (inert gas necessary) For boronizing Ni-based alloys
Ekrit		Cover material; prevents oxigen penetration into heating box

3.1.2. Seal Container

Seal container which is made of stainless steel with high chromium rate was used for placing specimens in boronizing treatments was shown in Figure 3.3.

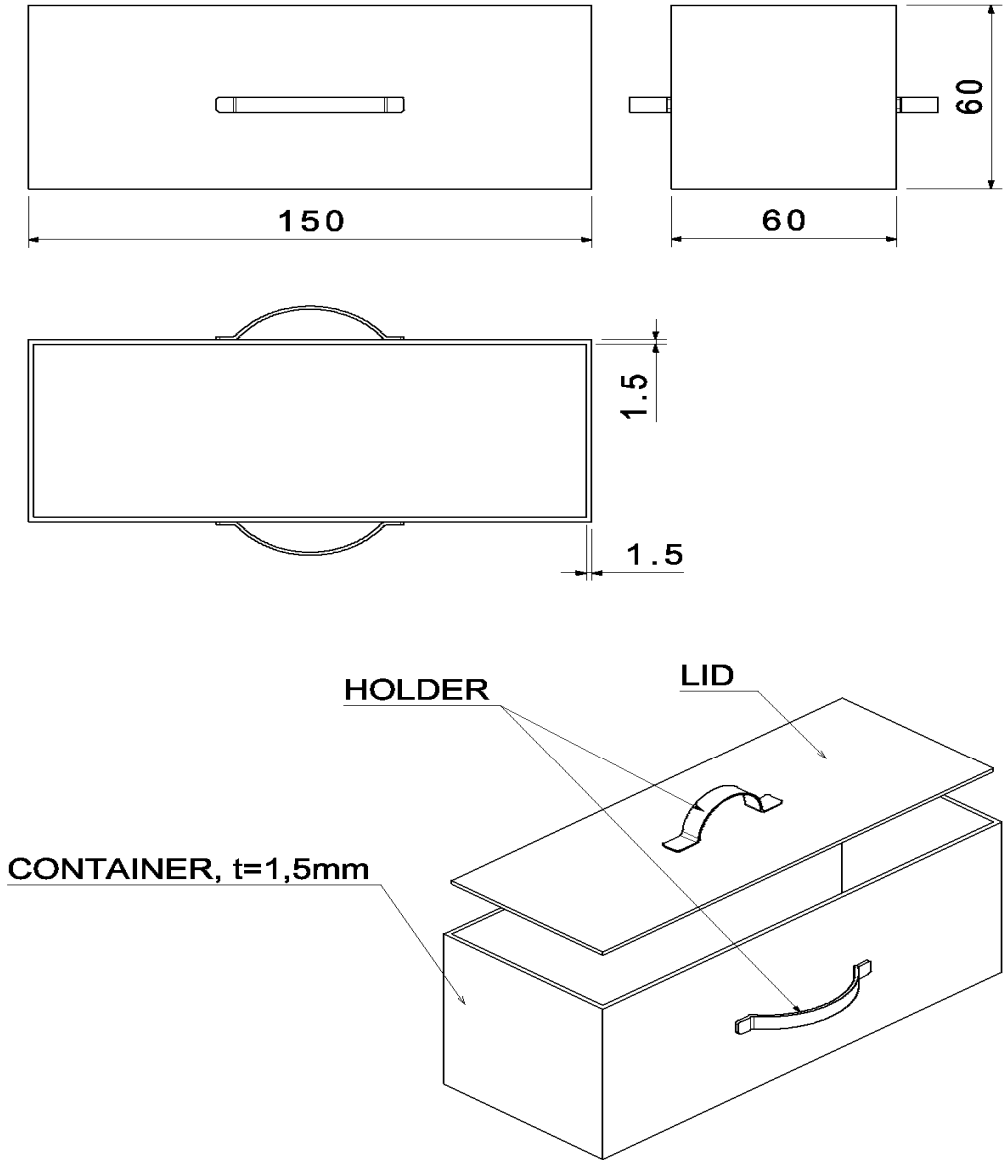

Figure 3.3. Seal Container used in boronizing processes

3.1.3. Corrosion Tests

CHI 604d Electrochemical analyzer device was used both for anodizing process and to obtain AC impedans curves with current-potential curves.

Reference Elektrode : Silver-silver chloride electrode (Ag,AgCl/Cl^-) were used as comparison electrode.

Solution: NaCl solution with %3,5 was used as a corrosion medium for specimens..

Counter Electrode : Bright platinum electrode which has surface area of 1x1 cm^2 is used as counter electrode

Working Electrode : Unboronized and borided specimens were used as working electrode. Copper wire that were pass through the specimen, were given in Figure 3.4.

Figure 3.4. Working electrode

Scanning Electron Microscope (SEM): In this study, SEM was used to study the surfaces of samples after the corrosion tests. SEM is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scanpattern, and the beam's position is combined with the detected signal to produce an image.

3.2. Method

Boronized specimens were analyzed using different experiments such as wear resistance, corrosion resistance, optical microscopy, thickness and microhardnes as follows.

3.2.1. Boronizing Treatment

3.2.1.1. Packing

Speciemens were packed in a seal container that contained the boronizing power mixture. 10 mm Ekobar 2 was poured into the plate. After specimens were placed in 10 mm intervals, again 10 mm ecobar 2 was poured on specimen. Sealing was carried out by applying refractory bricks around the tap of the plate by seen Figure 3.5. After the boronizing powder mixture was fully filled in the container, the container was sealed with a lid, and then placed in a preheated furnace.

Figure 3.5. Refractory bricks applied around the Seal Container

3.2.1.2. Process Parameter

Specimens were hold at 800 °C, 850 °C, 900 °C temperatures for 3, 6 and 9 hours. Then specimens were cooled in air after boronizing process. Then, specimens were removed from seal container and cleaned from ekobar 2 powder left on on the surface of the specimens using soft brush.. Six specimens were used for each experimental contions.

Also unboronized specimens were hold at 850 °C in 30 mimutes and then quenched to obtain martensitic structure for compasion purposes.

3.2.1.3.Furnace

Heating process of testing samples were conducted using electrical muffle furnace in Cukurova University Mechanical engineering Laboratory. The furnace shown in Figure 3.6 is HERAEUS KR 170 E type which has 100x170x260 mm combustion chamber, 1150 °C nominal temperature and 3 KW, 220 V, 50 Hz capacity. Digital control equipment was selected and mounted to this furnace to work in more sensitive temperature ranges during experiments.

Figure 3.6. Electrical muffle furnace used in the experiments

3.2.2. Hardness Test

The speciemens prepared for optical microscopy were reused for the hardness measurements. These were performed on a Vickers Hardness Tester. Vickers hardness measurement were taken on boronized specimens at room temperature in Cukurova University Mechanical Engineering Laboratory. BMS (Bulut Makine Sanayi) hardness measurement device, shown in Figure 3.7, with a minor load 1 kgf and a major load 4 kgf were used. Surface of specimen was cleaned for a sensitive measurement with alcohol then dried and indenter mark was made for each specimen surface at three distinct region. These marks were investigated by microscope of the machine.

Figure 3.7. Hardness Test Machine used for hardness measurements

The Vickers indenter is a square based pyramid with an angle of 136 degrees between the faces and a ratio of diagonals of 1:1 (as shown in Figure 3.8). The Vickers hardness number is one of the most widely used measures of hardness in engineering and science. The Vickers diamond hardness, VDH, is calculated using the indenter load and the actual surface area of the impression. The resulting quantity is usually expressed in kgf/mm^2 (Ziheng Yao, 2005). In this study, vickers hardness test was used under 5 kgf load.

F= Load in kgf

d = Arithmetic mean of the two diagonals, d_1 and d_2 in mm (Figure 3.8)

HV = Vickers hardness

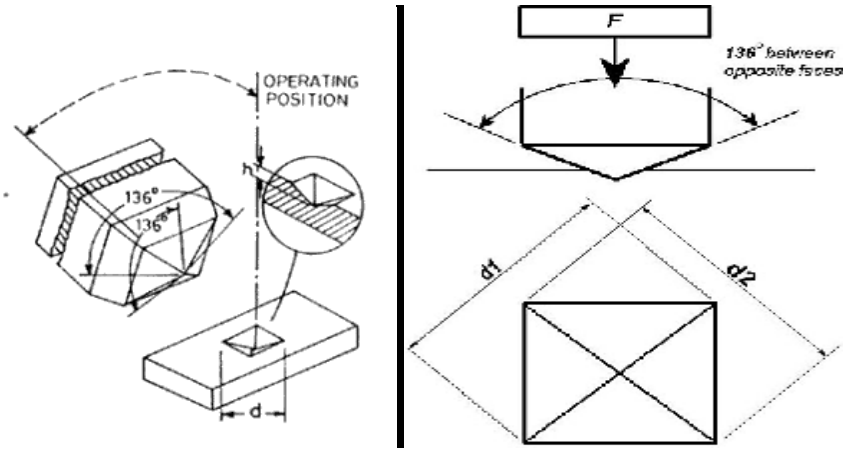

Figure 3.8. Scheme of Vickers hardness test and Vickers impression

$$HV = 1.854.\frac{F}{d^2} \tag{3.1.}$$

3.2.3. Optical Microscope and Thickness Measurements

Optical microscopy was used to examine the strucrure of boronized samples and to measure the coating thickness using a optical microscope with 1000X zoom capability. The boronized steels were sectioned to produce speciemens for the optical microscopy and thickness measurements. These speciemens were cleaned and moulded into Bakelite. Each speciemen was then grinded and polished using different grades of abrassive papers and aluminum suspension. Finally the speciemens were etched in 2% Nital solution, cleaned and dried. The images of boronized speciemens were used to study microstructure and thickness. Used optical microscope were shown in Figure 3.9.

Figure 3.9. Optical Microscope used in the study of microstructure

3.2.4. Wear Analyis

Available grinding machine that used for wear analysis, is modified as a pin on disc. Device as shown in Figure 3.10. The rotational speed of the device can be adjusted to either 300 or 600 times in a minute. The amount of applied loads at the device can be easily changed by adding or removing weights as shown in Figure 3.10.

Abrasive test was performed at dry conditions under constant load of 30 N. Al_2O_3 abrassive paper of 220 mesh was used as an abbrasive material. These abrassive papers were pasted to rotating part of machine by applying sticker to bottom surface. New abrassive paper was used for each specimen. Wear experiments were carried out in the laboratory at normal room temperature and humidity. Precisa 125A machine with a sensivity of 10^{-4} gr, was used to measure the changing in weights of the specimens after abrasion process.

Each specimen was cleaned by alcohol then dried after the test. Rotating speed of the disk was chosen as 300 rpm in all experiments and weight losses formed by abrasion, are measured after 300, 600, 900, 1200 , 1500 revolutions.

Wear testings were repeated three times and arithmetic mean values were evaluated. Since initial weight of each specimen were different from eachother,

weight losses were defined by using weight loss percentage calculated using the initial weight and the weigh measured at the end of the abrasion test to facilitate comparison at the same sample.

Figure 3.10. Modified grinding and polishing device for abrassion tests

3.2.5. Corrosion Resistance Test

Electrochemical corrosion process, shown in Figure 3.11 was used both for anodizing process and to obtain AC impedans curves with current-potential curves to investigate the corrosion resistance of coated speciemens.

Figure 3.11. Electrohemical corrosion process

Three different specimen groups were chosen for corrosion resistance tests. Specimens treated at 800 °C for 3 hours, at 900 °C for 6 hours and specimens that were not treated used in these tests.

Working electrode was cut 15 mm length then bottom area of electrode was drilled to put the copper wire inside of it for obtaining conductivity.

The other side of the electrode was coated with polyester block. Surface area of the prepared soft steel electrode was 190 mm^2.

Surface of the working electrodes were passed etanol, washed with pure water and sinked to %3,5 NaCl solution after dried with filter paper. Experiment was carried out in medium that was open to the atmosphere and at the normal room temperature.

3.2.5.1. Alternating Current Impedance Method (EIS)

Experiments were performed applying 10 mV amplitude in the frequency ranges of 10^5- 10^{-1} Hz in alternating current impedance technique at open circuit potential. Impedance measurements were taken for ranges of 4h, 24h, 48h, 72h and 144h. Obtained datas were then given as Nyquist, Bode and Phase angle diagrams.

3.2.6. Taguchi Analyis

Taguchi technique was used to optimize parameters by evaluating the results obtained from hardness and thickness tests..

Statistical performance measurement that is known as S/N ratio, was used to analyze results at this approaach which was developed by Dr. Genichi Taguchi. Results obtained during experiments, was converted to Signal / Noise (S/N) ratio then evaluated. Signal factor showed the real value that was obtained from system while noise factor show the factors that was not a parameter of the experiment, but affects the results of the experiment. Noise resources were variables which causes to deviation in the desired performace characteristics from target value. Therefore if N value is small, a value that is close to the desired target value, can be obtained. That is to say, aim is to maximize the S/N ratio at this analyze. Many S/N ratios are available in the literature. But “The biggest the best” criterion is used in this study for Nusselt (η).

$$\eta = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right) \tag{3.2}$$

Y shows performance characteristic value (Nusselt number) while n shows the number of Y values in Equation (3.2)

4. RESULTS AND DISCUSSIONS

4.1. Microstructure Studies

Boronized specimens were investigated for metallographic examinations under optical microscope in this research. Images of internal structure were taken and boron layer thickness was determined to examine changing in the structure after boronizing process. Images of microstructure belongs to 1050 steel that boronized in 800, 850 and 900 °C temperatures for 3,6 and 9 hours, are given in Figure 4.1- 4.3. It was seen that borides of surface of the boronized specimens had female morphology with different thicknesses depending on the process times and temperatures.

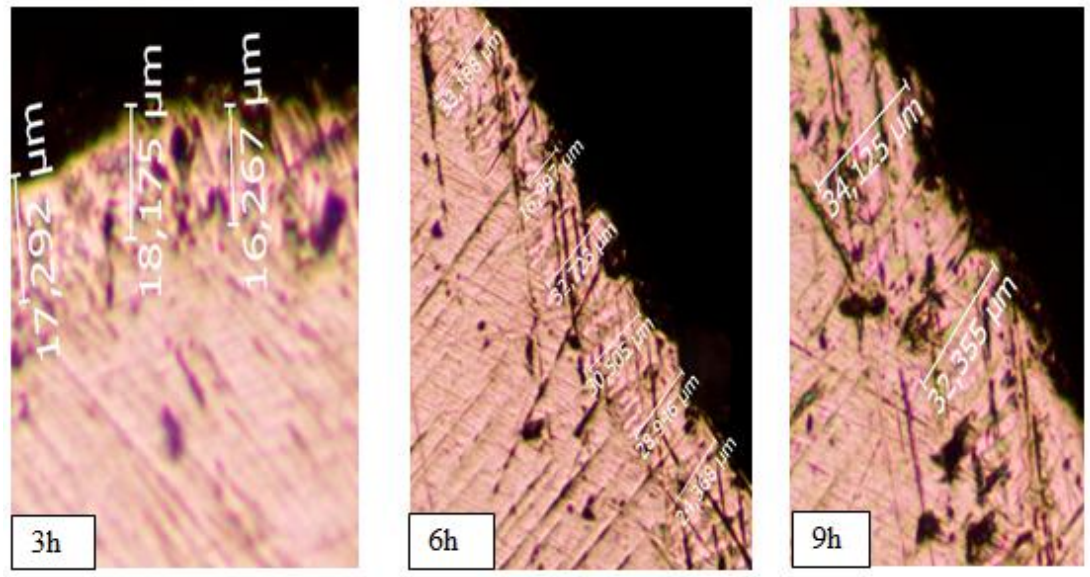

Figure 4.1. Thickness of boron layers belongs to AISI 1050 specimens that boronized at 800 °C for 3,6 and 9 hours

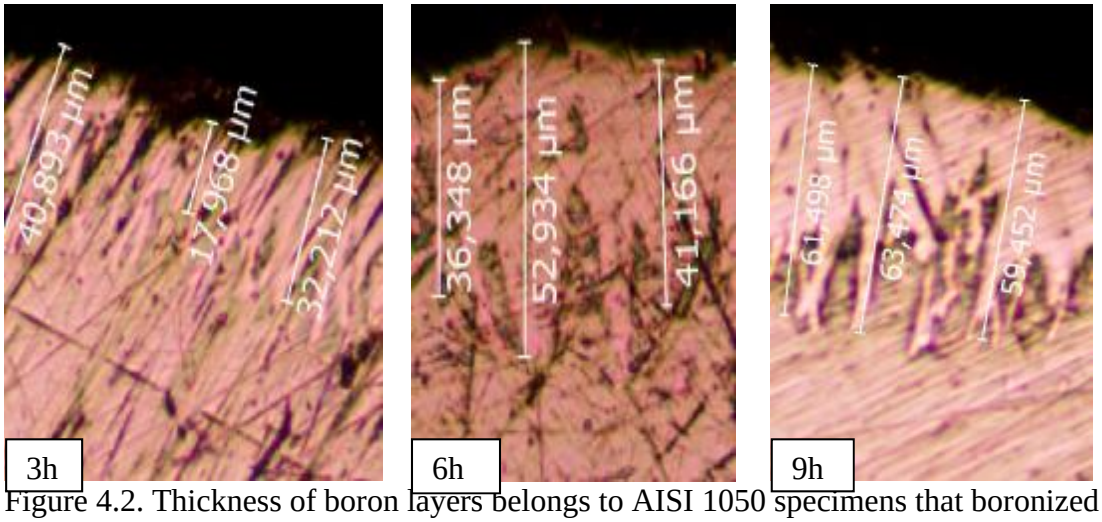

Figure 4.2. Thickness of boron layers belongs to AISI 1050 specimens that boronized at 850 °C for 3,6 and 9 hours

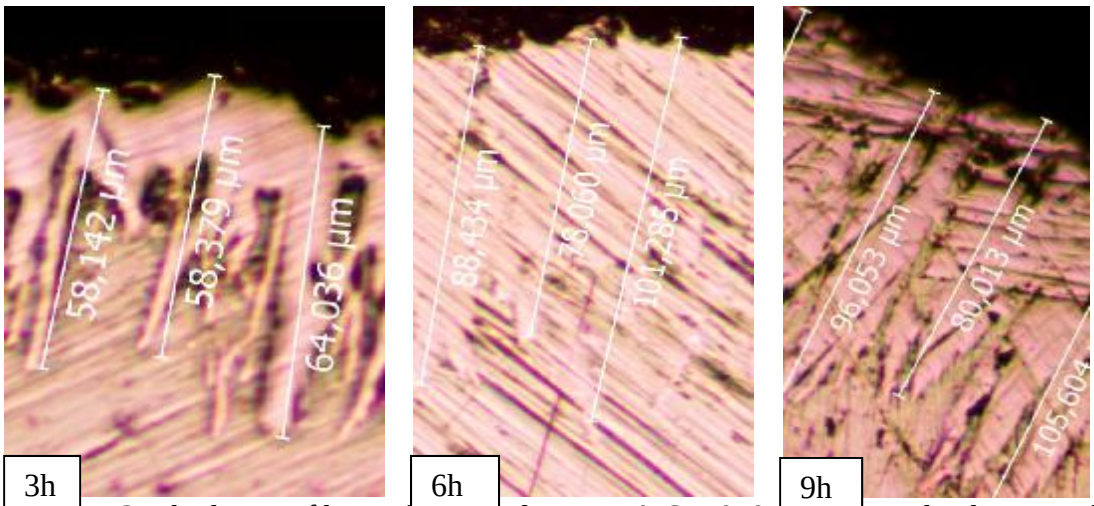

Figure 4.3. Thickness of boron layers belongs to AISI 1050 specimens that boronized at 900 °C C for 3,6 and 9 hours

Arithmetic mean value of thickness of boron layers obtained for each experimental set and the mean value of thickness of boron layers belongs to boronized specimens were given in Table 4.1.

Tablo 4.1. Mean value of thickness of boron layers belongs to boronized specimen

Thickness (µm)	3h	6h	9h
800 °C	17,3	28,6	31,6
850 °C	26,6	44,3	52,6
900 °C	49,6	79	96,6

It was observed that boron layer thickness was increased based on boronizing time and temperature as shown in Figure 4.4. The lowest boron layer thickness of 17,3 µm was obtained at 800 °C and 3h, the higher boron layer thickness of 96,6 µm was obtained for boronized specimens at 900 °C and 9h

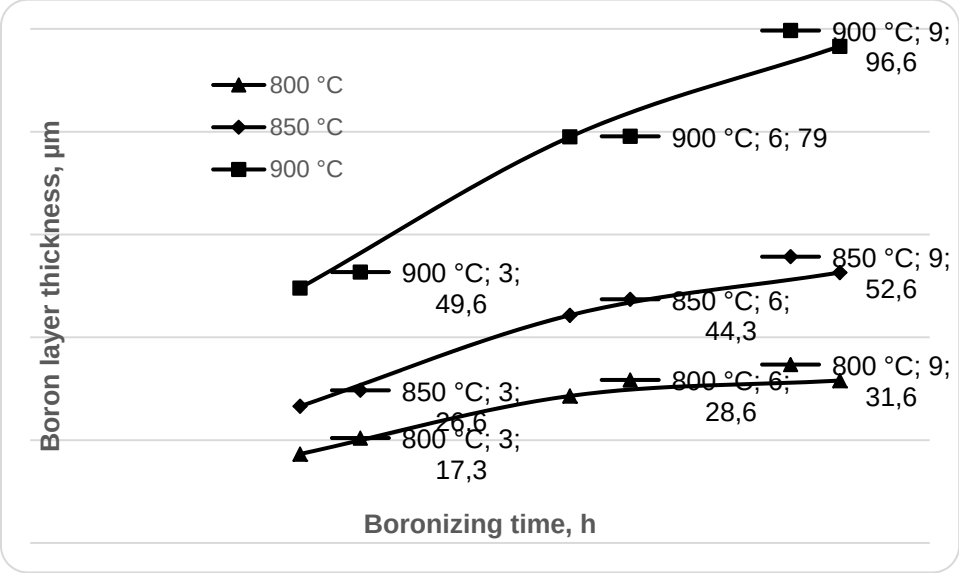

Figure 4.4. Variation of boron layer thickness in AISI 1050 steel for different boronizing temperatures and times

It was observed that specimens that boronized at different temperatures and times had nonhomogeneous saw tooth structure at the surface of material. Many of the researchers stated that boride layer of carbon steels that boronized by thermochemical methods, showed the similar saw tooth structure (Özbek I, 2000). Saw tooth structure is a characteristic property of boride layer. It has been shown that the amount of formation of tooth-shaped transition depends on not only process temperature and time but also alloy elements concentration between coating and base

material (Tabur M., 2008). It has been seen taht the layer thicknesses structure obtained in this work are compatible with literature.

Calık et al. (2014) examined AISI 1050 steel. The specimens together with the boronizing mixture were placed into an alumina crucible coated with a protective layer of Ekrit paste and held for 5 h in a resistance furnace at 900°C and atmospheric pressure. They have obtained the maximum layer thickness as 115 µm after boronizing process.

Er and Par (2004) have conducted boronizig process using AISI 1050 steel as a substrate material at 950°C for 2, 4 and 6 hours then they obtained boron layer thicknesses as 68,2 µm, 75,1 µm and 108,7 µm respectively. Increased in the holding time was accompanied with a increase in the layer thickness as obtained in this study.

4.2. Hardness

5 kgf of load was applied to test hardness value of boronized AISI 1050 steel speciemens. The marks that left by this load, were investigated under optical microscope and hardness valus were calculated. Images belongs to optical microscope, were given in Figures 4.5 – 4.7. Arithmetic mean of hardness values obtained from the hardness measurements are given in Table 4.2. The hardness of untreated AISI 1050 and heat treated AISI 1050 steel speciemens were also given in Table 4.3 for comparision purposes.

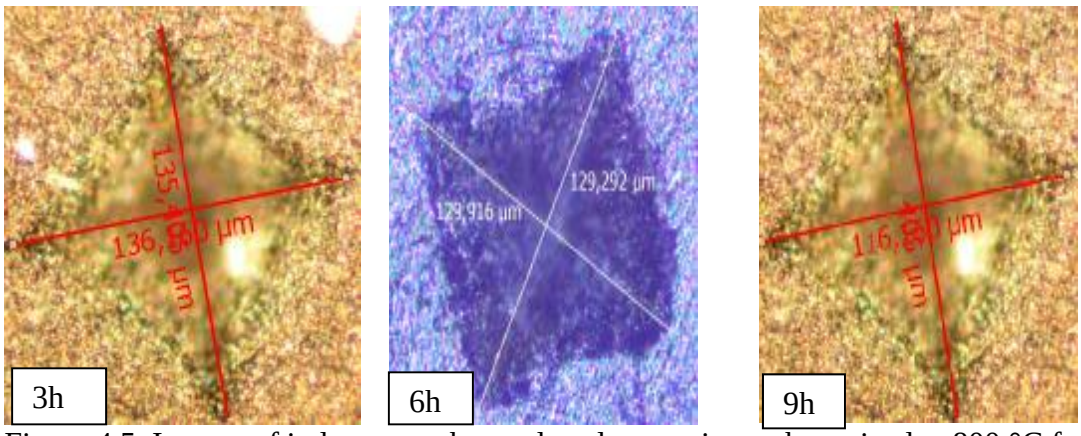

Figure 4.5. Images of indenter marks produced at specimens boronized at 800 °C for 3 6 and 9 hours

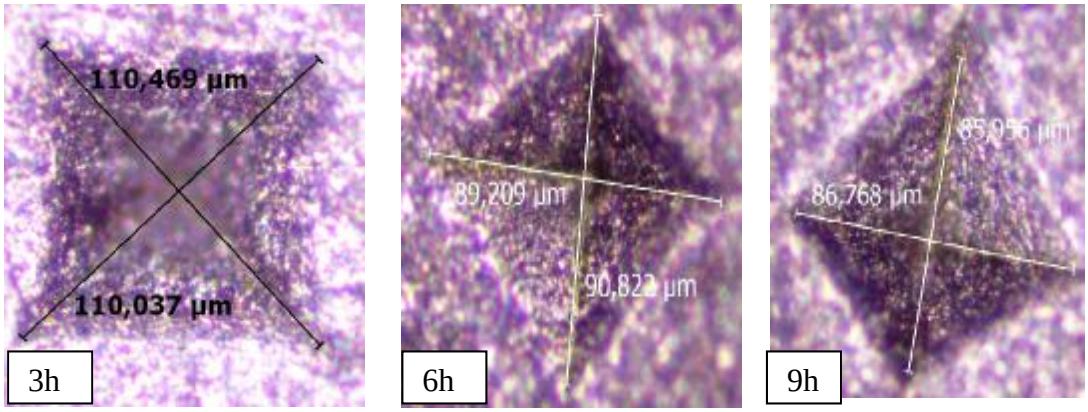

Figure 4.6. Images of indenter marks produced at specimens boronized at 850 °C for 3 6 and 9 hours

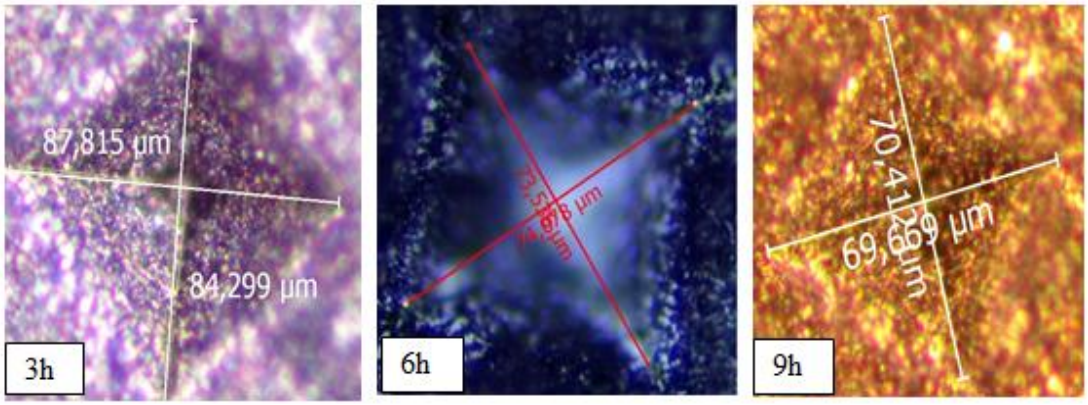

Figure 4.7. Images of indenter marks produced at specimens boronized at 900 °C for 3 6 and 9 hours

Table 4.2. Arithmetic mean of hardness values obtained at different conditions

Hardness (HV_5)	**3h**	**6h**	**9h**
800 °C	516	562	643
850 °C	762	1208	1256
900 °C	1550	1699	1886

Table 4.3. Hardness values measured at the unboronized and heat treated AISI 1050 steel

AISI 1050	**HV**
Unboronized	188
Heat Treatment	598

As seen in Table 4.2 and Figure 4.8, increase in hardness value were obtained by increasing boronizing time and temperatures. The highest hardness value belongs to specimens boronized at 900°C and 9h. This value is aproximately 10 times of hardness value of unboronized specimen and aproximately 3 times of hardness value of heat treated specimen.

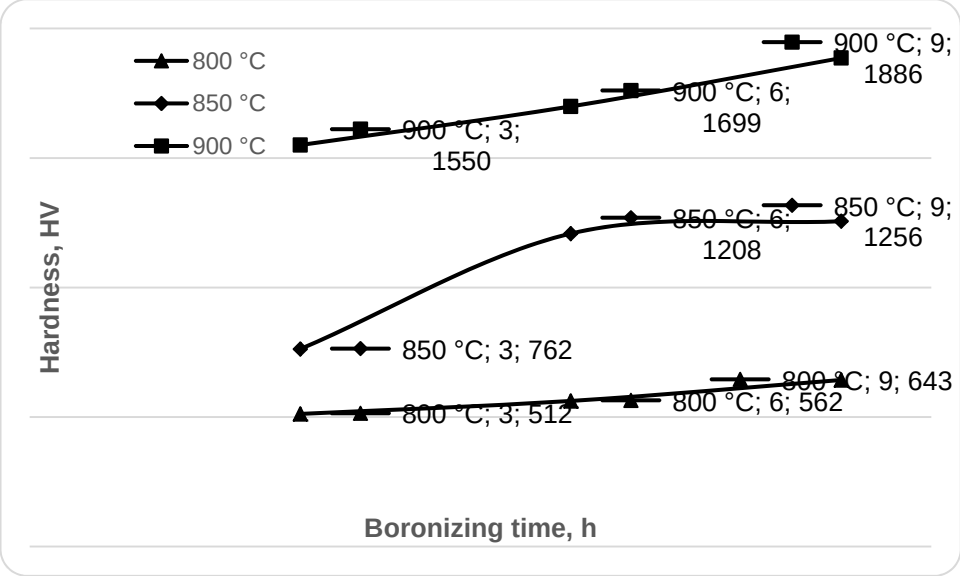

Figure 4.8. The relationship between hardness and boronizing parameters

The results obtained in this study are in good agreement with the previous works given in the following paragraphs.

Er U., and Par B., boronized AISI 1050 steel at 950°C and made measurement of hardness. When the holding time of specimens were increased from 2 hours to 6 hours, they determined that there were importanrt raisings in hardness and measured as 1504 HV-1716 HV at the end of 6 hours.

Calık et al. (2014) made hardness measurements by holding AISI 1050 steel at 900°C for 5 hours. They measured maximum surface hardness as 1950 HV, 550 HV in transition zone and 213 HV in matrix on specimens at the end of 5 hours.

Soydan et al. (2013) investigated AISI 1050 steel by boronizing at 950°C for 2, 8 hours and using Ekabor 1. They detected that hardness increased to 1800 HV at the specimens that boronized for 8 hours

4.3. Taguchi Analysis

Boron layer thickness and hardness values obtained at different conditions were analyzed by Taguchi method to determine the optimum hardness value and boron layer thickness for each temperature and time range. Signal to noise (SN) values were determined for hardness and boron layer thickness of specimens and given in Table 4.4. Since the maximum ratio is the best, it was aimed to maximize the S/N ratio in this analysis (E. Turgut, A. Dikici, 2011).

Table 4.4. SN values for hardness and boron layer thickness determined at different conditions

Temprature (°C)	Time (h)	$SN_{Hardness}$	$SN_{Thickness}$	$SN_{Hardness}$ (%)	$SN_{Thickness}$ (%)
800	3	54,2	24,5	-	-
800	6	54,9	29,1	1,2	18
800	9	56,1	29,9	2,1	2,7
850	3	57,6	28,5	-	-
850	6	61,6	32,9	6,9	15,4
850	9	61,9	34,4	0,4	4,5
900	3	63,8	33,9	-	-
900	6	64,6	37,9	1,2	11,7
900	9	65,5	39,7	1,3	4,7

Also values in the same temperature group were calculated to examine raising in SN values. 3 and 6 hours of boronizing time were taken as references respectively for investigation of 6 and 9 hours.

A significant increase was observed in thickness with percentages of 18 at 800 °C boronizing temperature in SN values. On the other hand increase in hardness with a percentages of 1,2 was obtained at the same speciemen. When the time were increased to 9 hours, amount of increases were 2,1 and 2,7 percents respectively for hardness and thickness. These results show that operating temperature of 800 C and 6 hours of holding time will be more economical since the increase in layer thickness

and hardnes values are not significant for the higher holding times at this boronizing temperature.

The most significant increase were occurred in the six hours partition at 850 °C. Amount of increase was 15,4% for thickness and 6,9 % for hardness. When the time were increased to 9 hours, it was observed that raising were only 0,4% in hardness and 4,5% in thickness. The working temperature is 850 °C and 6 hours holding time seem more economical because of significant increase in both hardness and thickness values.

The most significant increase were determined at thickness with 11,7% raising by the 6 hours of boronizing time at 900 °C boronizing temperature too. Only 1,2% increase in hardness was obtained at this temperature and holding time. When the time was increased from 6 to 9 hours, raising were %1,3 in hardness and % 4,7 in thickness. Again for this experiment setup it was determined that 6 hours of time were more economical due to others.

Incresing in boronizing time from 3 hours to 6 hours caused to serious raising in thickness of boron layer. But when the time were increased to 9 hours, it was seen that the rate of increase in hardness and layer thickness values were not significant due to very fast.diffusion speed of the boron element into material in 6 hours of time. Diffusion speed were decreased when the was increasen after 6 hours of holding time.

These results were observed more clearly when the above SN values are transmitted to graph,. Main effect plot for boron layer thickness based on time and temperature, interaction plot were given in Figure 4.9 and 4.10 respectively. Again changing of hardness based on temperature and time using SN values, were pointed out as main effect and interaction in Figure 4.11-4.12.

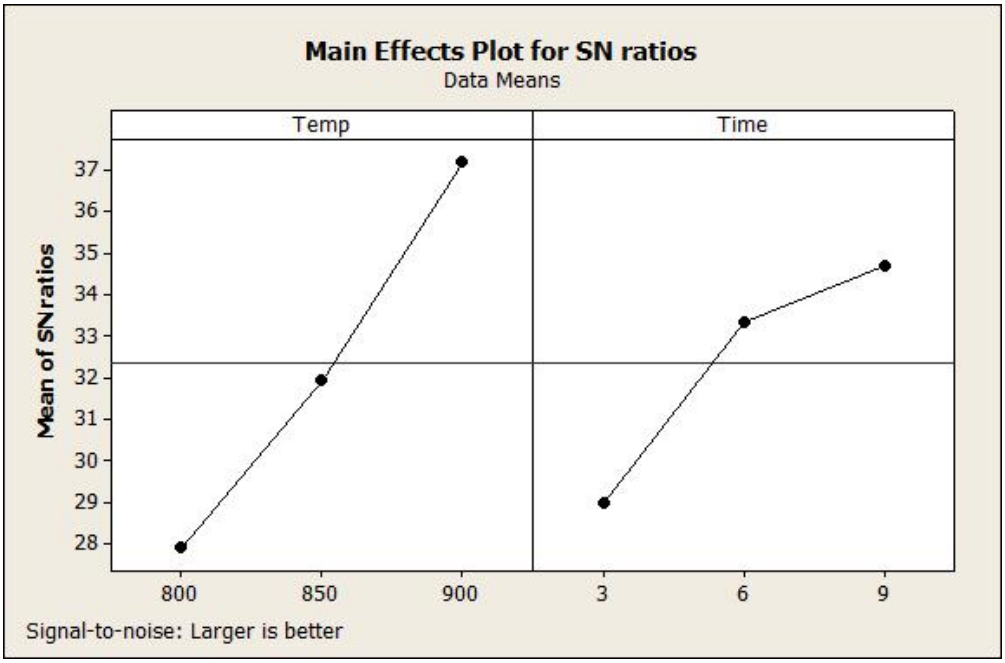

Figure 4.9. Main effect plot for boron layer thickness

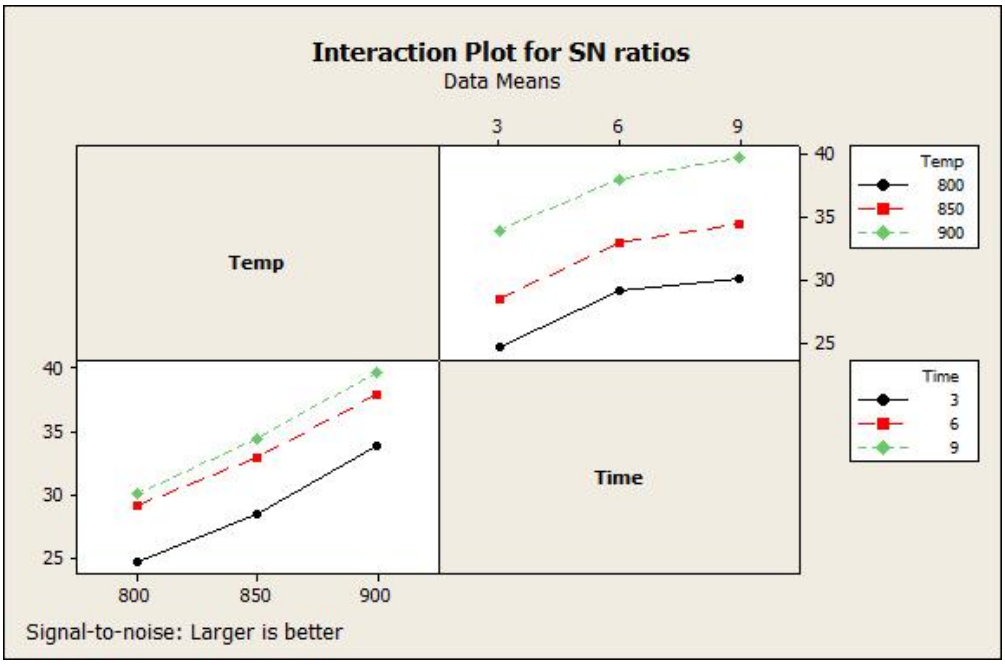

Figure 4.10. Interaction graph for boron layer thickness

It was seen that temperature and time affected the boron layer thickness in positive direction when the graphs were investigated. There was increment in the amount of increase in the thickness by rising the temperature to 900 °C. But the rate of increase were declined when the time was increased from 6 hours to 9 hours.

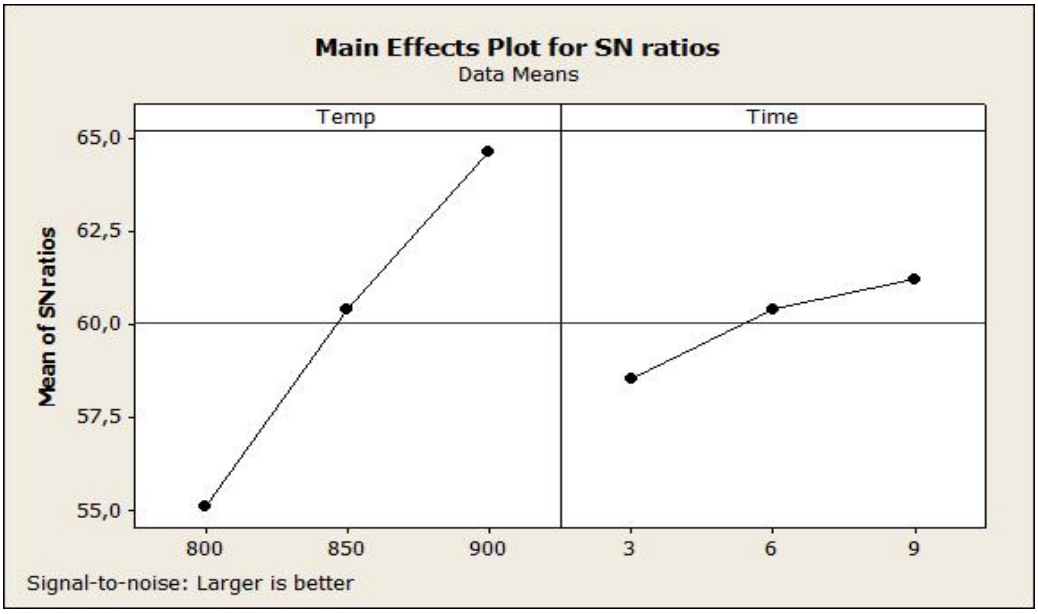

Figure 4.11. Main effect plot for hardness

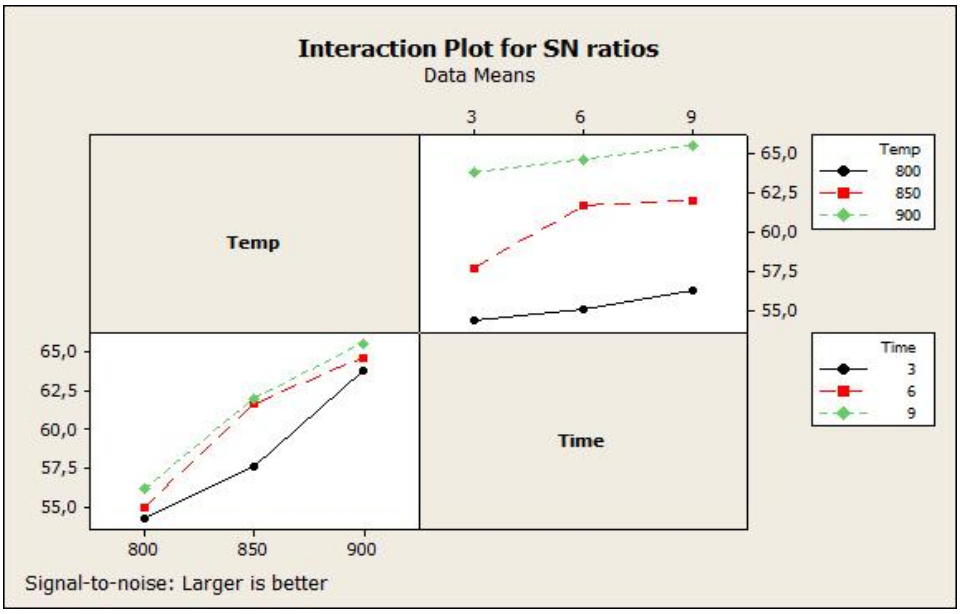

Figure 4.12. Interaction plot for hardness

It was determined that the rate of increase in hardness was high until 850 °C for 6h when the above graphs were investigated for hardness variation. It was also observed that the rate of increase were decreased by raising in temperature and time.

4.4. Wear Analysis

Specimens with and without boron, also the specimens held at 850 C and ½ hour then quenched, were used for abrasion wear tests. Consecutive total of the percentage of weight loss that were obtained from abrasion wear tests are given in Table 4.5- 4.8. Percentage of weight loss of specimens obtained at the end of each abrasion wear test, are plotted in Figure 4.13 for comparision purposes.

Table 4.5. Unboronized material and heat treated material that quenched

Percentages of weight loss after each rev. based on the initial weight (mg x 10^{-3})					
AISI 1050	300 rev.	600 rev.	900 rev.	1200 rev.	1500 rev.
Unboronized	255.32	350.28	412.39	490.74	560.53
Heat Treatment	105.14	160.25	225.41	280.22	426.23

Table 4.6. AISI 1050 specimens boronized at 800 °C for 3, 6, and 9h

Percentages of weight loss after each rev. based on the initial weight (mg x 10^{-3})					
AISI 1050	300 rev.	600 rev.	900 rev.	1200 rev.	1500 rev.
800 °C x 3h	110.17	170.12	230.45	300.56	445.36
800 °C x 6h	100.15	155.89	201.74	230.55	270.62
800 °C x 9h	87.13	101.53	120.28	154.19	192.79

Table 4.7. AISI 1050 specimens boronized at 850 °C for 3, 6, and 9h

Percentages of weight loss after each rev. based on the initial weight (mg x 10^{-3})					
AISI 1050	300 rev.	600 rev.	900 rev.	1200 rev.	1500 rev.
850 °C x 3h	98.36	153.68	189.57	221.42	260.58
850 °C x 6h	62.38	98.39	110.47	138.98	160.14
850 °C x 9h	43.25	79.24	95.64	108.31	133.82

Table 4.8. AISI 1050 specimens boronized at 900 °C for 3, 6, and 9h

Percentages of weight loss after each rev. based on the initial weight (mg x 10^{-3})					
AISI 1050	300 rev.	600 rev.	900 rev.	1200 rev.	1500 rev.
900 °C x 3h	59.74	79.55	98.65	108.28	122.65
900 °C x 6h	35.12	47.23	57.96	65.85	71.54
900 °C x 9h	34.63	45.96	56.52	60.73	64.61

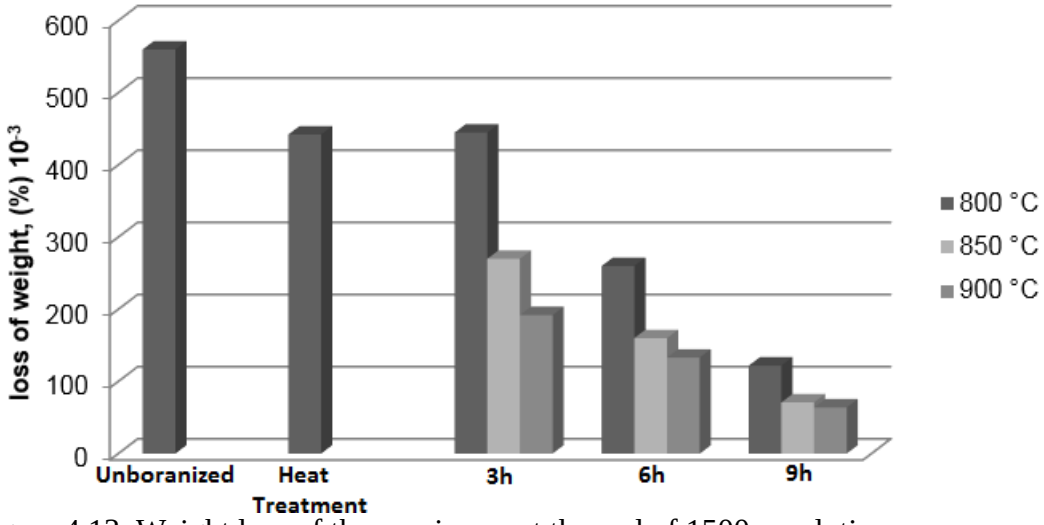

Figure 4.13. Weight loss of the specimens at the end of 1500 revolution

The results showed that the boronized AISI 1050 plain carbon steel gained very high ratios of abrasion wear resistance against the aluminum oxide abrasives used in the experiments due to increase in surface hardnes.

Increase in boronizing process time at any temperature resulted higher layer thickness and consequenltly caused less amount of wear at the boronized material. Maximum wear resistance were obtained at a higher boronizing temperature and time used in this study.

It has been seen that specimens which were boronized at 900 °C and 9h, had 8.75 times better wear resistance than untreated specimen and had 6.6 times better wear resistance than heat treated specimen when 1500 revolutions.

Also it was observed that wear resistance of the specimens that boronized at 800 °C for 3 hours resulted nearly the same resistance against wear with the hardened specimen. As given in the following paragraphs the results obtained in this work are compatible with literature.

Er et al. (2004) boronized AISI 1050 steel at 950°C and subjected to abrasion test. They found percantages of weight loss as 56,34 mg x 10^{-3}, 53.14 mg x 10^{-3}, 56.74 mg x 10^{-3} in specimens that boronized at 2, 4, and 6 hours respectively at the end of 1500 revolutions. On the other hand weight loss were found as 434.97 mg x 10^{-3} in unboronized AISI 1050 steel at the end of 1500 revolutions

4.4. Corrosion Analyis

Impedance curves which was obtained from corrosion test carried out on the untreated and boronized AISI 1050 steels at 800 °C for 3h and 900 °C for 6h in % 3,5 NaCl solution, was given in Figure 4.14 - 4.16 Impedance graphs was gained measuring 4, 24, 48, 72 and 144 hour intervals. Corrosion resistances of the specimens were decreased depending on time. The specimens that has the biggest corrosion resistance were seen in specimens that were boronized at 900 °C and 6h at the end of 144 hours. The lowest corrosion resistance was occurred at unboronized AISI 1050 steel.

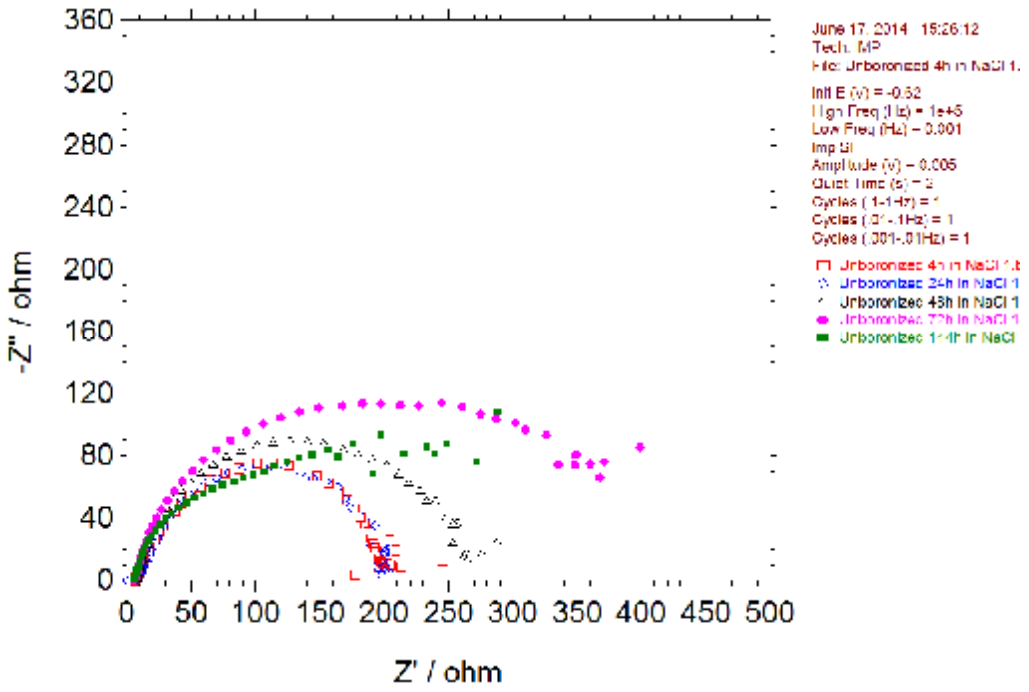

Figure 4.14. Impedance curves for unboronized AISI 1050 steel

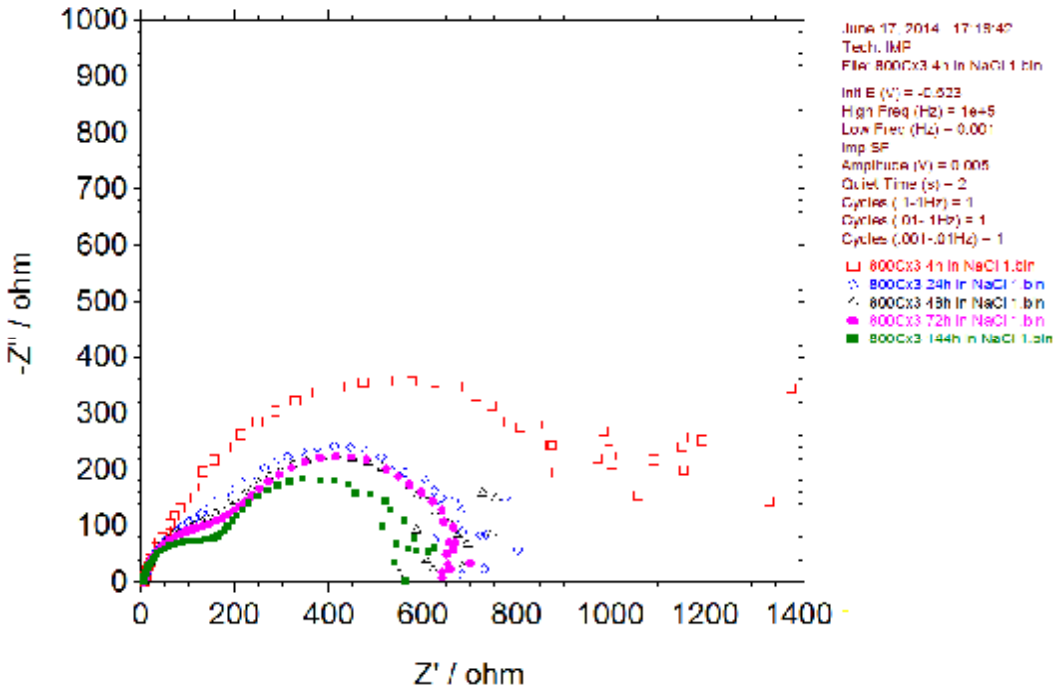

Figure 4.15. Impedance curves for AISI 1050 steel boronized at 800 °C and 3h

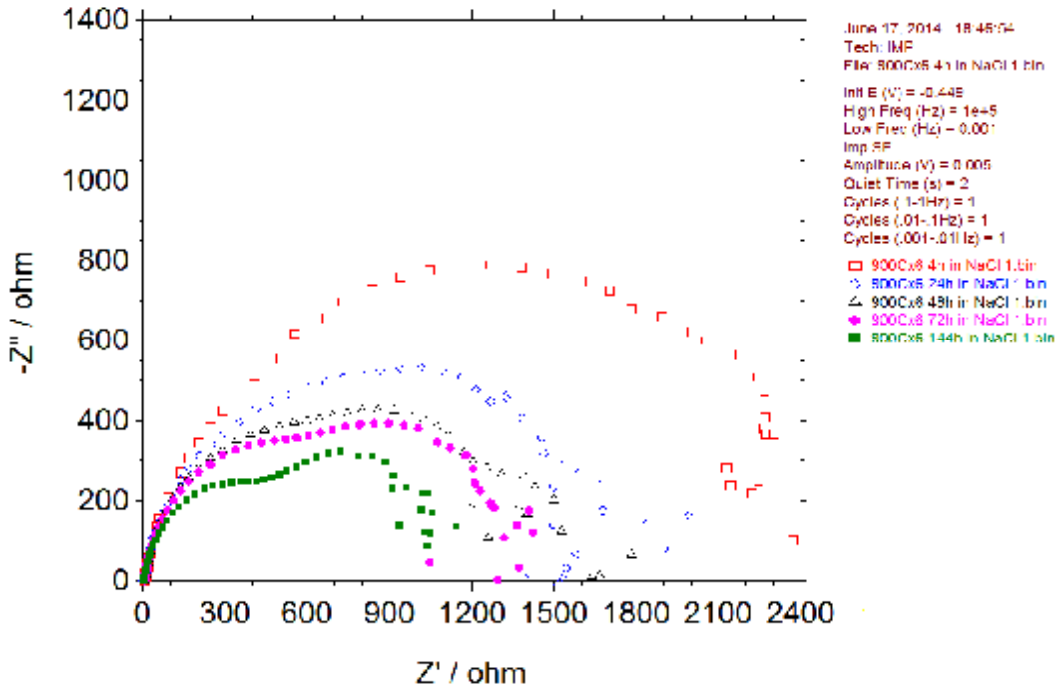

Figure 4.16. Impedance Curves for AISI 1050 steel boronized at 900 °C and 6h

Frequency and resistance curves belongs to specimens were given in Figures 4.17 – 4.19 Also polarization resistances were calculated and given in Table 4.9.

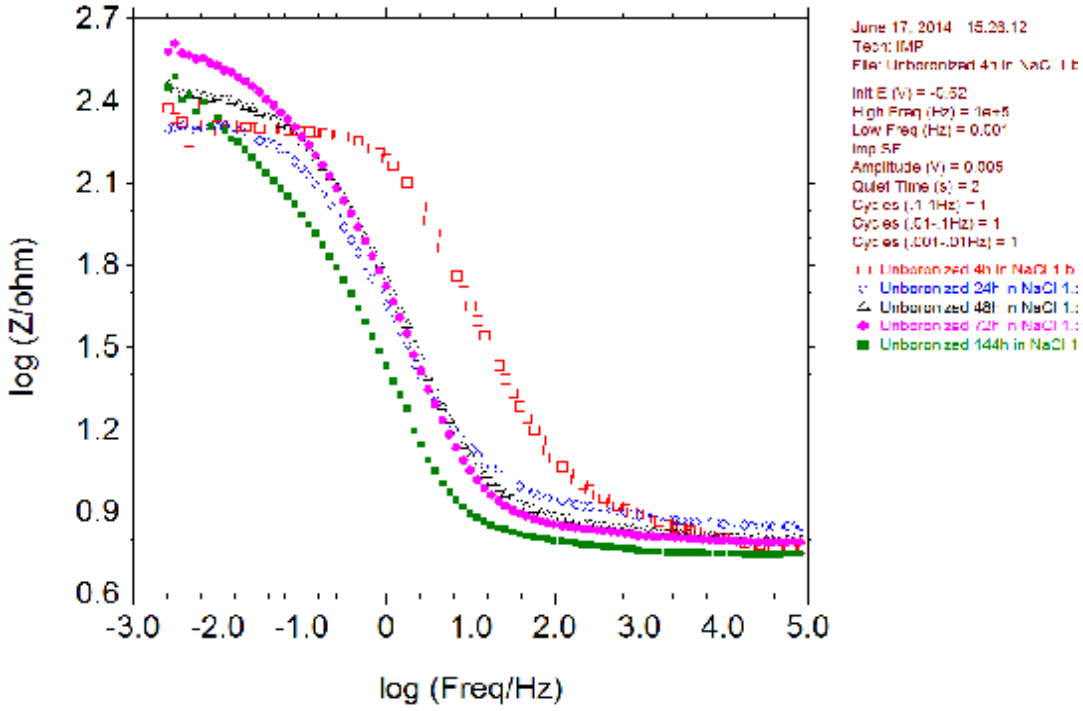

Figure 4.17. Impedance Curves for unboronized AISI 1050

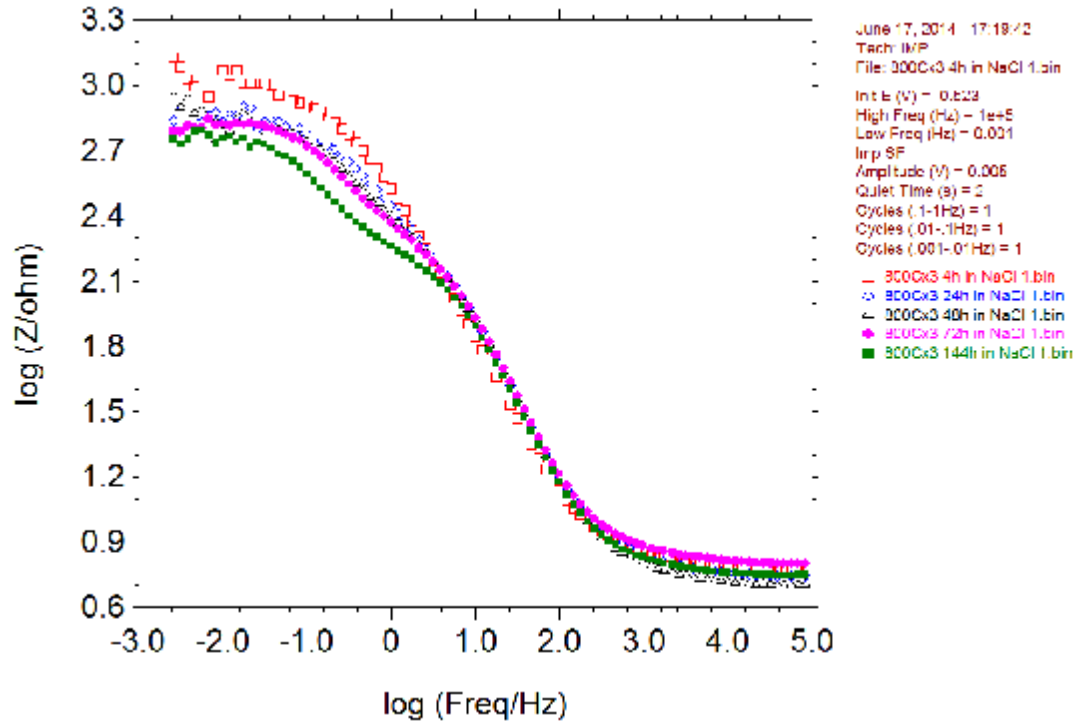

Figure 4.18. Impedance Curves for AISI 1050 steel boronized at 800 °C and 3h

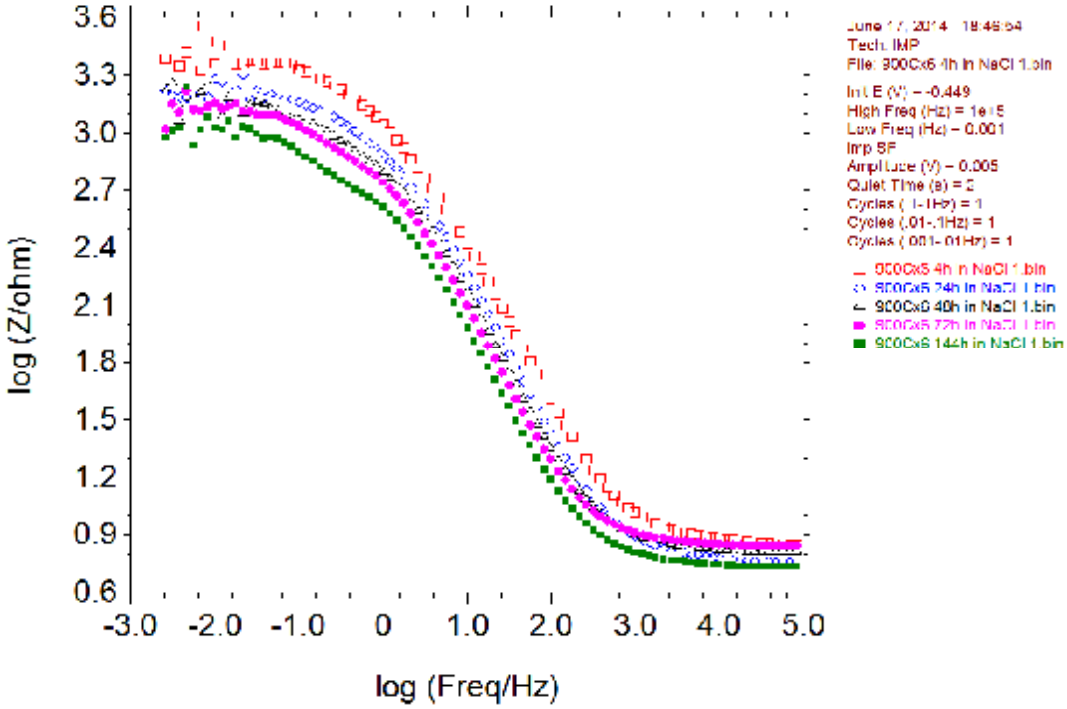

Figure 4.19. Impedance Curves for AISI 1050 steel boronized at 900 °C and 6 hours

Table 4.9. Polarization Resistances of Specimens (R_p)

Time (h)	R_p (ohm)		
	Unboronized	800 °C x 3h	900 °C x 6h
4	200	1288	2398
24	210	758	1905
48	295	630	1621
72	389	575	1174
144	436	545	1023

The higher the polarization resistance, the higher in the resistance to corrosion. It is determined that the specimens boronized at 900 ^{0}C and 6 hours had 2 times better corrosion resistance than specimens boronized at 800 ^{0}C and 3 hours and 5 times better corrosion resistance than unboronized specimens when Rp values were investigated at the end of 144 hour of testing time. As shown in Table 4.9 polarization resistances of untreated speciemen were increased and polarization resistances of boronized speciemens were decreased when the time is icreased. This is due to more stable oxide layer formatin in the untreated speciemen compared to boronized speciemens.

Phase angles of the same specimens obtained from the corrosion tests are shown in Figure 4.20-4.22. As seen in these Figures, the phase angle of 58^0 for unboronized specimen, 60^0 for specimens boronized at 800 ^{0}C and 3 hours and 70^0 for specimens boronized at 900 ^{0}C and 6 hours were obtained at the end of 144 hours of testing time.

There is a relationship between phase angle and corrosion resistance. Corrosion resistances of the specimens can be evaluated by looking phase angles. If the phase angle increases, corrosion resistance increases too. Therefore, it could be stated that the speciemens treated at 900 ^{0}C for 6 hours resulted better corrosion resistance due to larger layer thickness obtained at the end of the boronizing process.

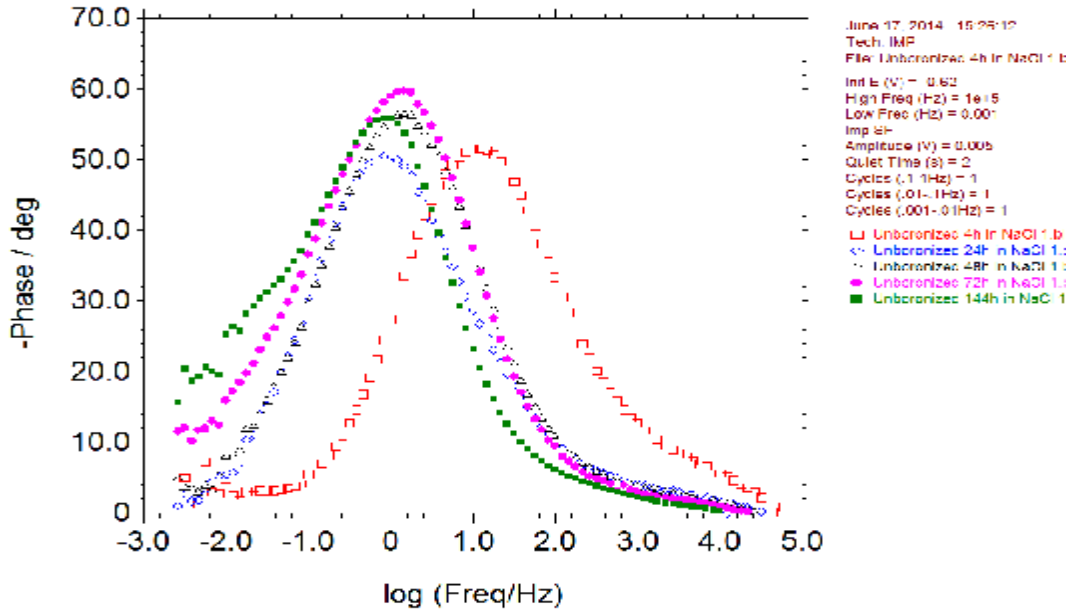

Figure 4.20. Phase angle of unboronized AISI 1050 steel

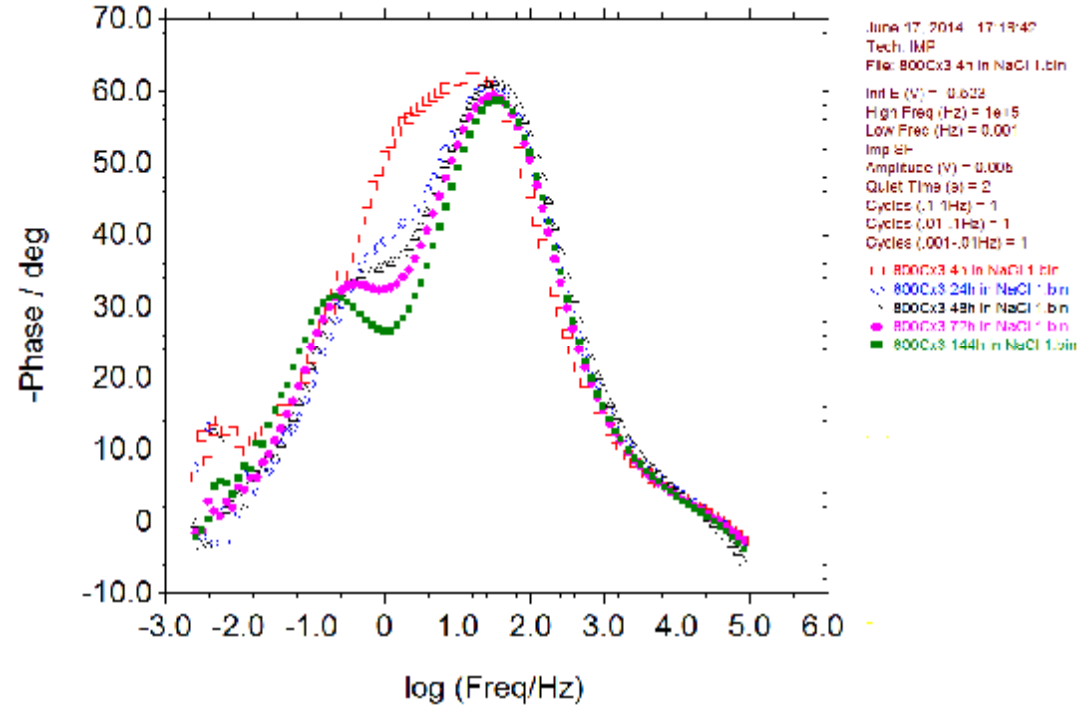

Figure 4.21. Phase angle of AISI 1050 steel boronized at 800 °C and 3h

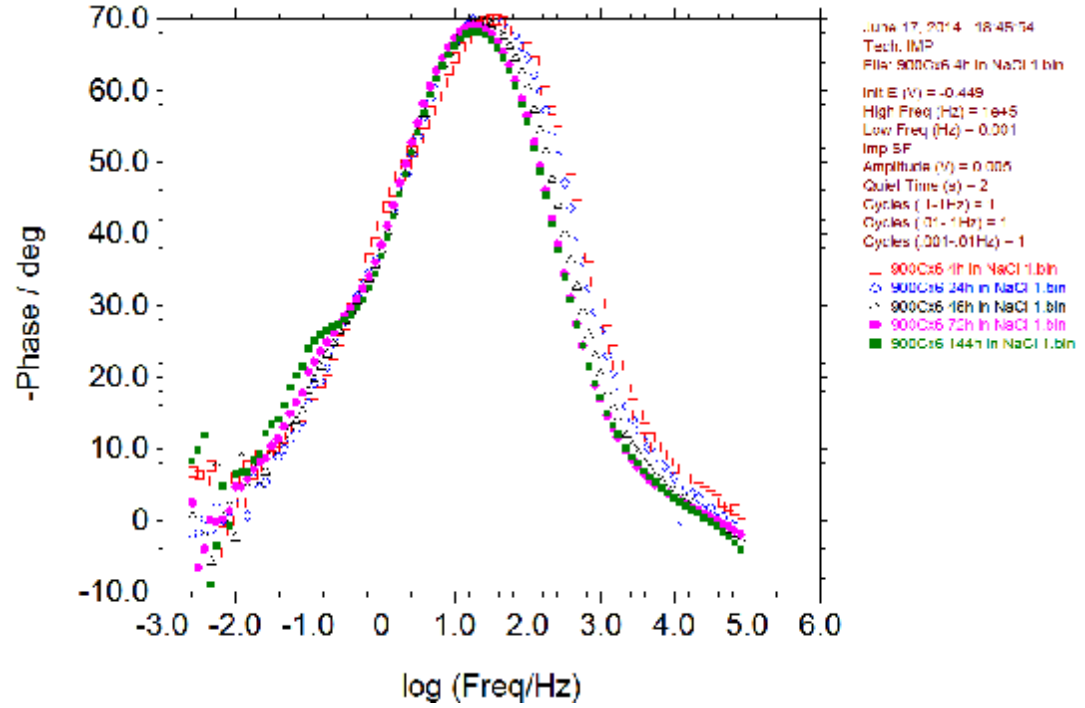

Figure 4.22. Phase angle of AISI 1050 steel boronized at 900 °C and 6h

Tafel curves were obtained by giving high amount of current at the end of corrosion test. Corrosion potentials (E_{corr}) of unboronized material, boronized 800 ^{0}C

for 3h and 900 ^{0}C for 6h were measured as -0,635, 0,505 and 0,313 respectively as given in Figure 4.23. It has been observed that boron caused to slip more positive values at corrosion potentials. This shows that the positive values value of boronized AISI 1050 steel at 900 ^{0}C for 6h dissolves in the solution at the more positive values compared to other samples given in the figure. This will show that the corrosion resistance of boronized specimens is higher at 900 °C and 6h. Due to higher layer thickness obtained at this conditions.

Atık et al. (2003) subjected boronized plain carbon steels to corrosion test. They also observed that the corrosion resistance of boronized specimens were increased when the boronizing time.was increased.

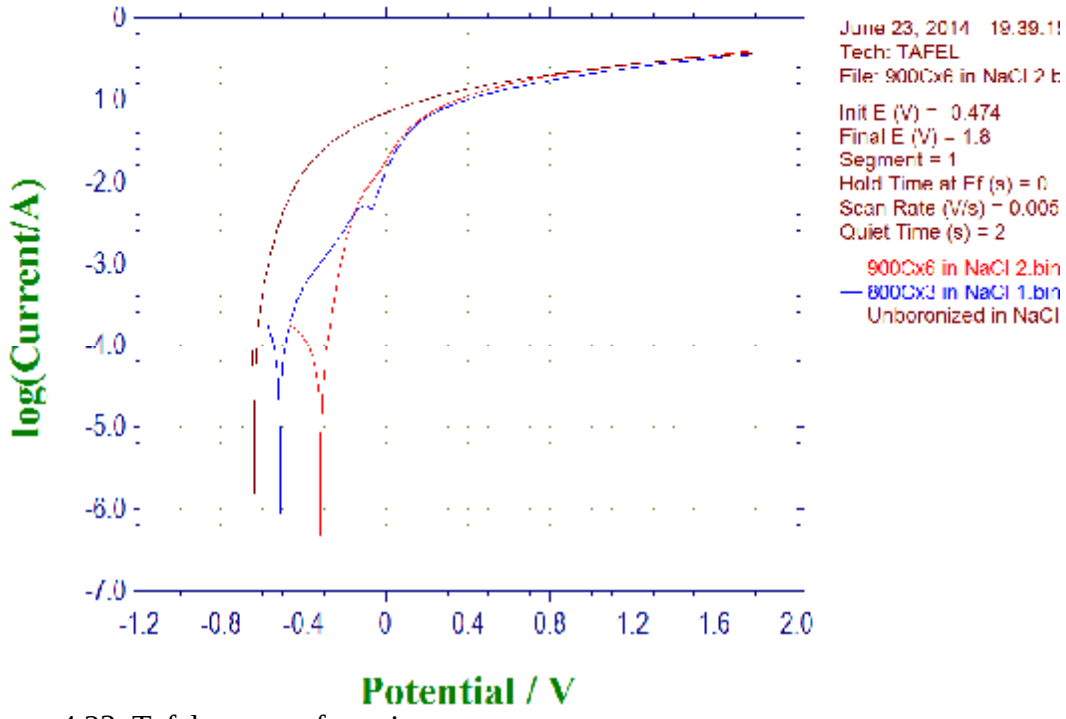

Figure 4.23. Tafel curves of specimens

SEM images taken from the untreated and treated speciemens at the end of 144 hours of corrosion tests are given in Figure 4.24-4.26. Oxide layer was seen too much in unboronized specimens. Distribution of this layer on surface were more unstable and it had rough surface compared to other specimens. It was seen that boronized specimens had more resistance against the oxide layer formation on

surface and more homogeneous oxide layer distribution. Therefore, on boronized speciemens less amount of oxide layer and smooth surface were obtained after the corrosion tests.

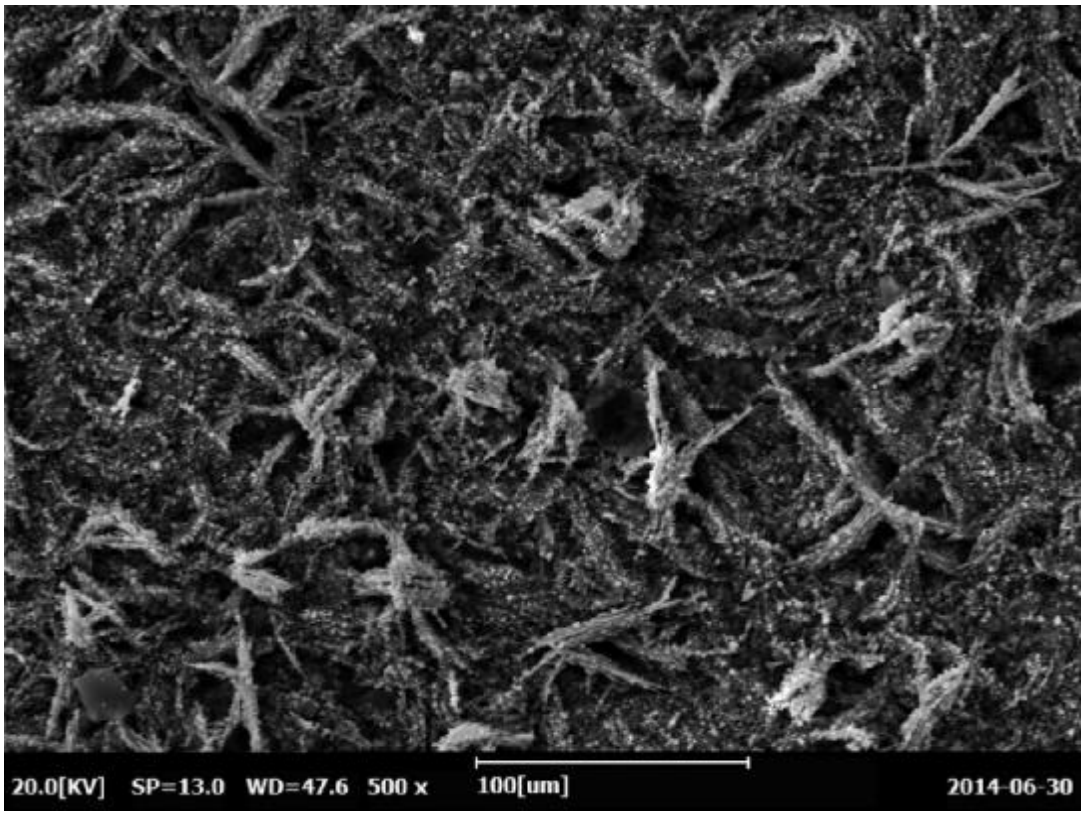

Figure 4.24. SEM image of unboronized specimen

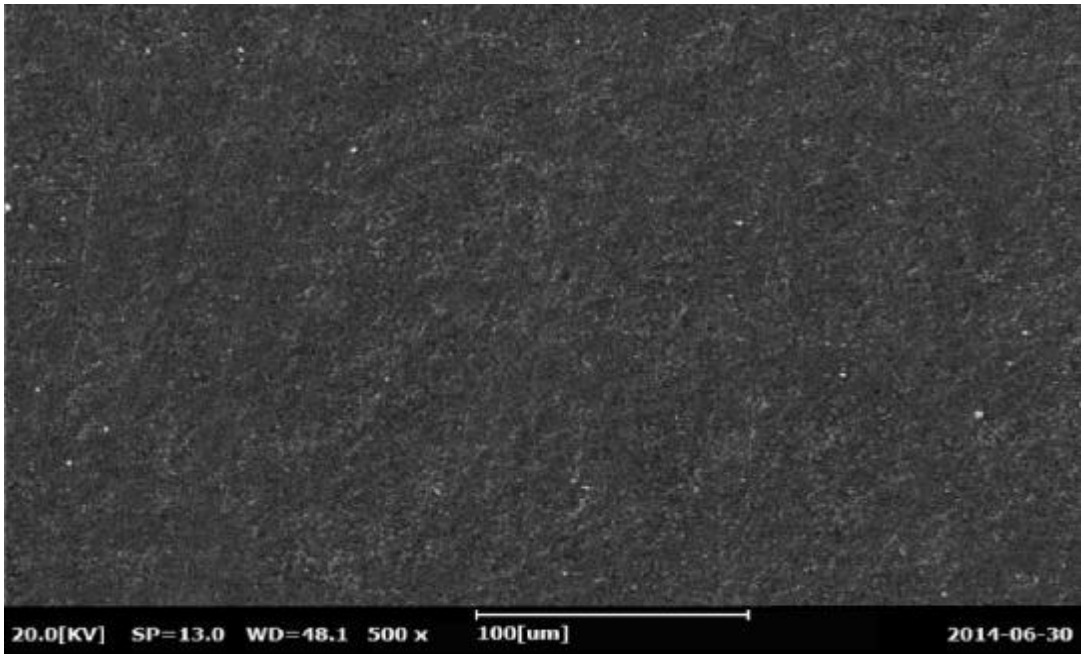

Figure 4.25. SEM image of specimen boronized at 800 °C and 3h

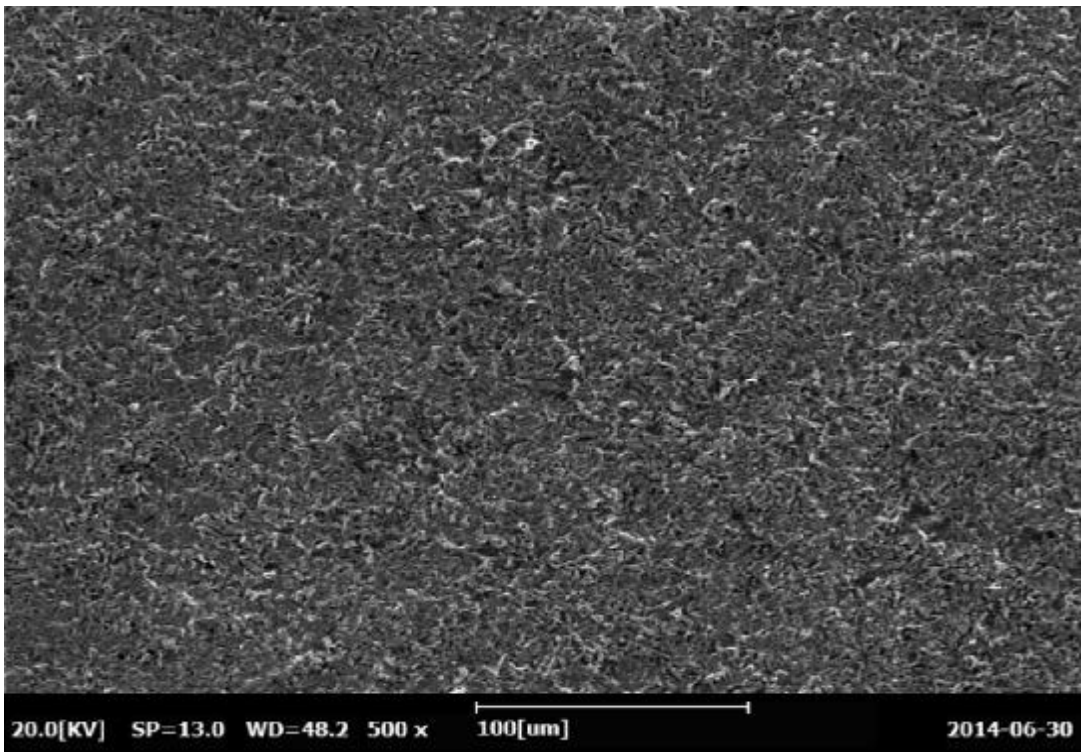

Figure 4.26. SEM image of specimen boronized at 900 °C and 6h

5. CONCLUSION

In this study, the surface of AISI 1050 steel has been treated by pack boronizing process at a temperature of 800, 850 and 900 °C with a time duration of 3, 6 and 9 hours. Characterization studies have been made to boronized steels and metallographically examined. Hardness, abrasion experiments and corrosion tests have been made. The conclusions that is obtained from these works are as follow;

1- While the boronizing temperature and time duration of specimens increases the thickness of boron layer increases. The highest layer thickness, 110 μm, was obtained for AISI steel at 900 °C and for a time duration of 9 hours. The minimum layer thickness, 17 μm, was obtained for AISI steel at 800 °C and for a time duration of 3 hours. The increasing of temperature and time allow to boron atoms to make more diffusion to the material. Therefore the form of saw teeth have become more apparent.
2- After the boronizing process the highest hardness value was obtained as 1886 HV_5 at 900 °C and 9 h. And the minimum hardness value was obtained as 516 HV_5 at 800 °C and 3 h.
3- Abrasion experiments have been carried out on the un treated, boronized and only hardened speciemens. The minimum resistance to abrasion was observed on the untreated specimens. The maximum resistance to abrasion was observed at a condition of 900 °C and 9 h for the boronized specimens. At the end of 1500 cycles the specimen that is boronized at 900 °C and 9 h showed significant difference considering the specimen that is subjected to only hardening treatment. The reason for this can be explained with the increased hardness and layer thickness according to the increased boronizing temperature and time duration.
4- When the boronizing time of specimens were increased from 3 to 6 hours, The results of Taguchi analysis showed that there were a significant increase in layer thickness for all processes.. The same rate of increase were not

obtained when the time were increased to 9 hours. On the other hand raising in hardness were observed by the increase in time. Important increase was seen in both hardness and thickness at 850 °C and 6h.

5- It is understood that boron layer significantly affects the corrosion resistance. A significant difference between boronized (800 °C for 3h and 900 °C for 6h) and unboronized specimens have been observed in the corrosion test. The maximum corrosion resistance was obtained for the boronized specimen at 900 °C and 6h. The increasing boron layer thickness resulted an increase in the corrosion resistance. Less and more homogeneous oxide layer were obtained on the surface of the boronized speciemens. On the other hand, cracks and rough surface have been observed on the SEM figures of non processed specimens taken after corrosion tests.

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