

## KINETIC INVESTIGATION OF AISI 304 STAINLESS STEEL BORONIZED IN INDIRECT HEATED FLUIDIZED BED FURNACE

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### Abstract

In this study, kinetic examinations on boronized AISI 304 Stainless Steel samples were described. Samples were boronized in indirect heated fluidized bed furnace consists of Ekabor 1™ boronizing agent at 1123, 1223 and 1323 K for 1, 2 and 4 hours. Morphologically and typically examinations of borides formed on the surface of steel samples were studied by optical microscope, scanning electron microscope (SEM) and X-Ray diffraction (XRD). Boride layer thickness formed on the steel X5CrNi 18-10 ranges from 12 to 176 μm. The hardness of the boride layer formed on the steel X5CrNi 18-10 varied between 1709 and 2119 Hv<sub>0.1</sub>. Layer growth kinetics were analyzed by measuring the extent of penetration of FeB and Fe<sub>2</sub>B sublayers as a function of boronizing time and temperature. The kinetics of the reaction has been determined with  $K = K_0 \exp(-Q/RT)$  equation. Activation energy (Q) of boronized steel X5CrNi 18-10 was determined as 244 kJ/mol.

**Keywords:** Boronizing; AISI 304; Indirect heated fluidized bed furnace; Kinetics of boron

### 1. Introduction

Boron is a group 13 element exist among metals and non-metals according to its properties. It has the symbol “B”, atomic number 5, atomic weight 10.81 u, empirical atomic radius 90 pm and melting temperature 2365 K [1, 2].

Boronizing is a thermoreactive diffusion surface treatment that has been defined in the German Industrial Standard DIN 17014 as “enrichment of the surface of a work piece with boron by means of thermo-chemical heat treatment” [3]. By means of thermal energy, boron atoms diffuse into the metallic lattice of the surface of a work piece, where they form borides with the atoms of the base material. When applied to the appropriate materials, boronizing provides wear and abrasion resistance. Boronizing increases resistance to acids, hydrochloric acid in particular, can be uniformly applied to irregular shapes and increases tool life [4].

A fluidized bed consists of a mixture of fluid and solid that exhibits fluid-like behavior. Fluidized beds are used as a technical tool which has the ability to promote high levels of contact between gasses and solids. A fluidized bed furnace is a cylindrical vertical vessel with an air or nitrogen feed at the bottom of the unit. A fluidized bed furnace may have great advantages over the other types of heat sources. When these beds are activated, they behave very similar to a boiling liquid bath. This provides rapid heat transfer to all directions equally. Also, fluidized bed furnaces are easy to maintain, inexpensive to run

and relatively safe to operate [5].

Industrial boronizing can be applied to most steels such as structural steels (AISI 1014, 1045, and 4140) as well as to austenitic stainless steels [6]. Thus, boronizing has been used to improve the surface properties of valves, burner nozzle, etc., in the industrial applications as boride layers have higher hardness, oxidation resistance, strong indicator of wear resistance and fracture strength [7, 8].

### 2. Experimental procedure

In this study, the X5CrNi 18-10 stainless steel was used for the boronizing treatment. Chemical composition of the steel sample is given in Table 1. Prior to the boronizing treatments, cylindrical specimens (Ø 10 x 15 mm) were prepared.

The boronizing of the specimens were carried out in a solid medium using the powder pack method. In this method, commercial Ekabor 1™ was used as boron source. The test samples and powder pack were heated in indirect heated fluidized bed furnace under 99.9 % pure nitrogen atmosphere at atmospheric pressure and 1123 K, 1223 K, and 1323 K for 1h, 2h and 4h as three different process time. After this process, the boronized samples were removed from the furnace and cooled in air.

Afterwards, the boronized steels were prepared metallographically by 80 to 1200 grit emery paper and then polished using diamond paste. The polished samples were etched with Royal Water (mixed in a 1:3

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**Table 1.** The chemical composition of the test material

AISI Number	Alloying Elements (% Weight)										
	C	Mn	Si	P	Cr	Ni	Mo	Co	V	W	Al
304 (X5CrNi 18-10)	0.05	1.06	0.5	0.04	20.41	7.96	0.15	-	0.07	0.11	-

ratio of  $\text{HNO}_3:\text{HCl}$ ) prior to testing. The microstructure was examined by optical microscope (Leica ICM 1000) and SEM (Model JSM-5410 LV). The average thicknesses of the boronized layers were measured using an image analyser unit.

The Vickers microhardness measurements were carried out from the surface to the substrate along a respective cross-section using a microhardness tester with a load of 100 g.

The presence of borides formed on specimen surfaces were analyzed by a Philips Panalytical X-Pert Pro diffractometer with a  $\text{Cu K}\alpha$  radiation source with a wavelength of  $1.541 \text{ \AA}$  over a  $2\theta$  range from  $20^\circ$  to  $90^\circ$ .

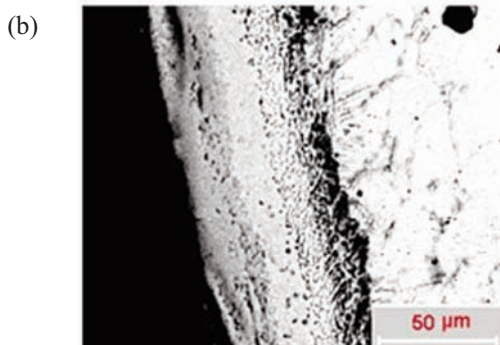
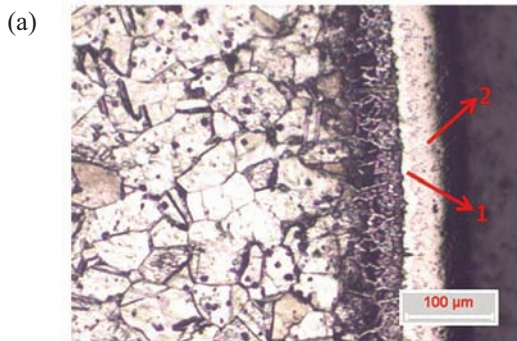
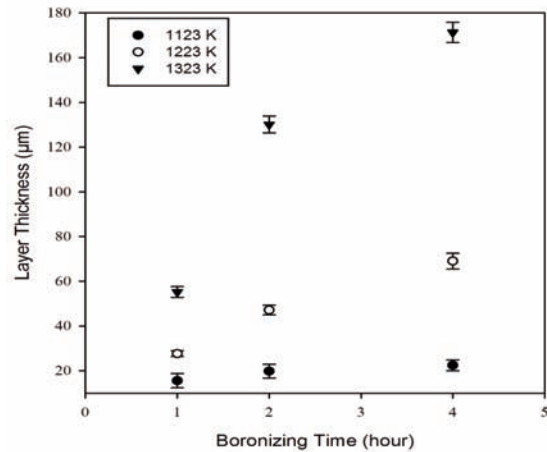
### 3. Results

#### 3.1. Microstructure and hardness observations

As seen in Fig. 1, optical and SEM examinations revealed that the borides formed on the surfaces of the specimens have a columnar morphology.

Three distinct regions were identified on the surface of the specimens: borides, transition zone and matrix. The boride layers formed on boronized steel have columnar morphology and the prolonged boronizing

time and higher temperatures result in thicker boride layers.  $\text{Fe}_2\text{B}$  layer thickness increased with an increase in the boriding time because the boriding kinetics is a thermally activated phenomenon [9]. The SEM micrograph of the boride layer formed on the X5CrNi18-10 steel, composed of  $\text{FeB}$  and  $\text{Fe}_2\text{B}$  phases. Outer phase of the layer is  $\text{FeB}$  and inner phase is  $\text{Fe}_2\text{B}$ . This phases definable by contrast differences. On the microstructure image in Fig. 1,  $\text{Fe}_2\text{B}$  phase (white) is shown with the number 1 and  $\text{FeB}$  phase (gray) is shown with the number 2. In the present investigation, the boride layer formed on X5CrNi 18-10 steel samples ranged from  $12,3 \mu\text{m}$  to  $175,8 \mu\text{m}$ . This can also be seen from Fig. 2. as well as Table 2. After the microscopic examinations, the hardnesses of the samples were determined by Vickers hardness method. Vickers microhardness measurements are shown in Fig. 3 and their values are listed in Table 3.

**Figure 1.** Microstructure of boronized steel X5CrNi 18-10 a) optical microscope, b) SEM (BEI)**Figure 2.** Thicknesses of boride layer on X5CrNi 18-10**Table 2.** Boride layer thicknesses on X5CrNi 18-10

Boronized Material (AISI)	Boronizing Temperature (K)	Boronizing Time (hour)	Boron Phase Layer Thickness ( $\mu\text{m}$ )
304	1123	1	$15,5 \pm 3,2$
		2	$19,8 \pm 3,1$
		4	$22,4 \pm 2,4$
	1223	1	$27,6 \pm 1,3$
		2	$47,1 \pm 2,2$
		4	$69,0 \pm 3,5$
	1323	1	$55,2 \pm 2,4$
		2	$130,1 \pm 3,7$
		4	$171,3 \pm 4,5$

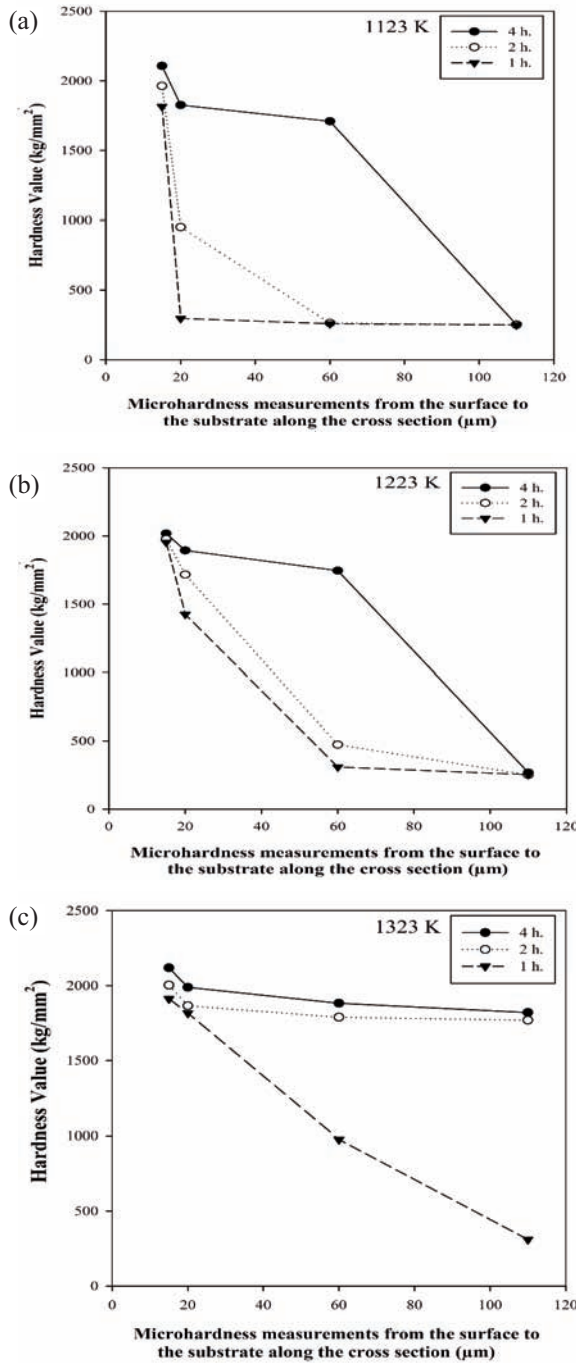


Figure 3. Microhardness measurements of the boronized samples. (a) 1123K, (b)1223K, (c)1323K

3.2 XRD observations

Fig. 4 shows the XRD patterns of the specimens boronized at a temperature of 1123 K, 1223 K and 1323 K for 1 h. The boronized layers mainly consisted of FeB and Fe<sub>2</sub>B. Furthermore, small amounts of Cr<sub>2</sub>Ni<sub>3</sub>B<sub>6</sub> and Ni<sub>2</sub>B phases were found.

Table 3. Microhardness of the boronized steel X5CrNi 18-10

AISI 304 / Hv <sub>0,1</sub>		Boronized Layer Depth			
		15μm	20μm	60μm	110μm
1123K	4 h.	2107	1826	1709	252
	2 h.	1963	952	263	250
	1 h.	1816	296	258	249
1223K	4 h.	2018	1894	1746	268
	2 h.	1978	1717	473	251
	1 h.	1953	1425	309	253
1323K	4 h.	2119	1989	1883	1821
	2 h.	2004	1866	1790	1770
	1 h.	1913	1817	977	310

3.3 Kinetic examinations

The layer thickness of the boronized samples varies parabolic with time according to the following equation [10, 11]

$$x = \sqrt{Kt} \tag{1}$$

with x: boronized layer thickness in cm, t: boronizing time in s and K: growth rate constant in cm<sup>2</sup>/s. If the kinetics of layer formation for the periods between 1h and 4h are considered, it can be recognized that the square of boride layer thickness changes linearly with time, as it can be seen in Fig. 5.

The relationship between the growth rate constant, K in m<sup>2</sup> s<sup>-1</sup>, the activation energy, Q in j×mol<sup>-1</sup>, and the process temperature, T in K, can be expressed as an Arrhenius equation [11]

$$K = K_0 \times \exp\left(-\frac{Q}{RT}\right) \tag{2}$$

With K<sub>0</sub>: frequency factor and R: gas constant in j×mol<sup>-1</sup>×K<sup>-1</sup>. Taking the natural logarithm of Eq.(2) leads to the following Eq.(3):

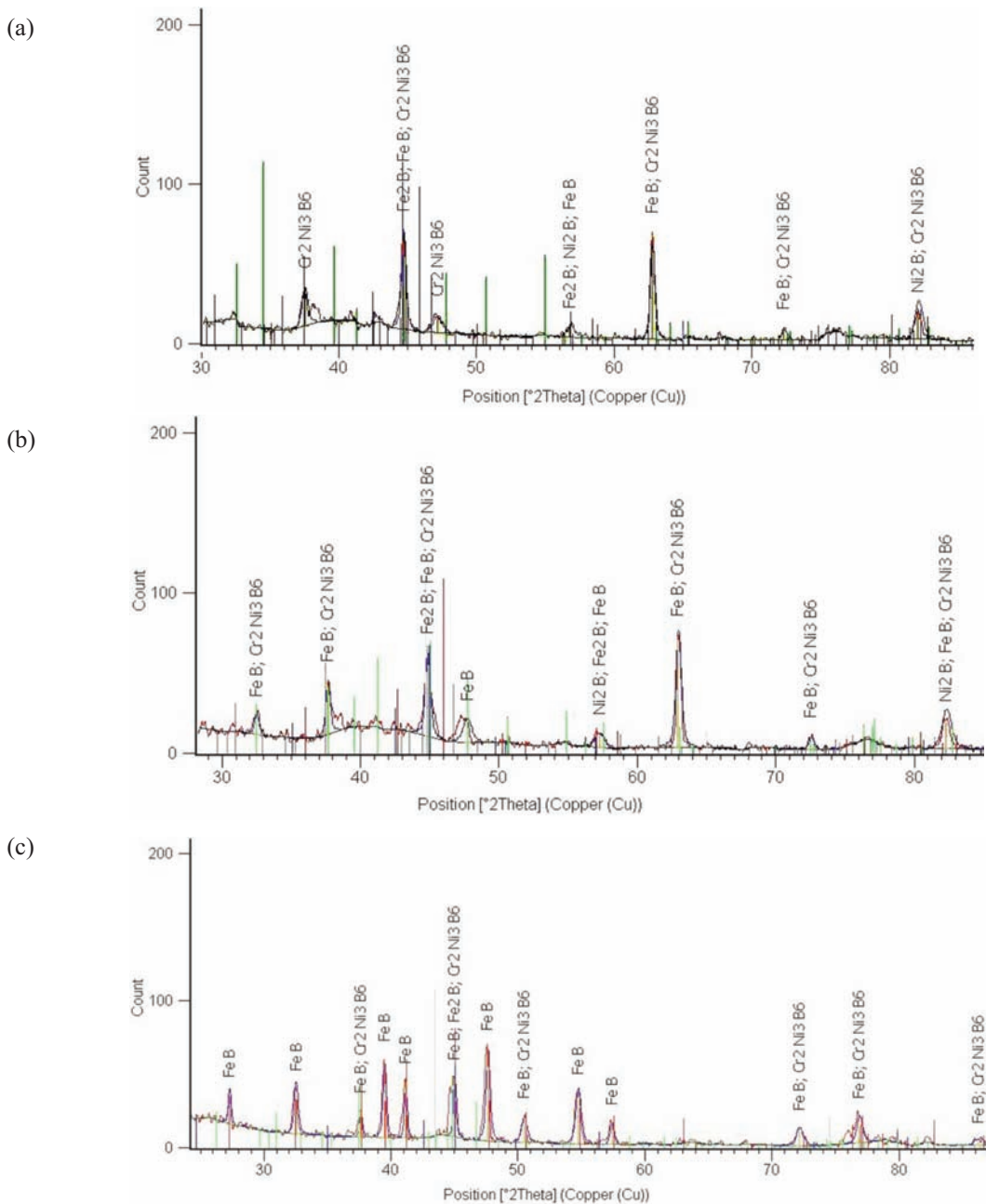
$$\ln(K) = \ln(K_0) - \left(\frac{Q}{RT}\right) \tag{3}$$

The activation energy for the boron diffusion in the boride layer is determined by the slope obtained by the plot ln(K) vs. 1/T, using Eq. (3). The plot of ln(K) vs. reciprocal boronizing temperature is shown to be linear, as can be seen in Fig. 6.

The activation energy Q and the constant K<sub>0</sub> were determined from the slopes of straight lines obtained at 1/T=0 by setting the intercept of the extrapolated straight lines to the abscissa as origin; as can be seen in Table 4.

Table 4. Activation energy, frequency factor, and diffusion depth of boronized steel X5CrNi 18-10

Boronized Material	Q (kj/mol)	K <sub>0</sub>	x (cm)
X5CrNi 18-10	244	9.21	9.21 exp (29317/T) × t



**Figure 4.** X-ray diffraction patterns of boronized steel X5CrNi 18-10 (1h.) at different temperatures, a)1123K, b)1223K, c)1323K

#### 4. Discussion

The X5CrNi18-10 stainless steel specimens were boronized with powder pack method in the range of 1123 – 1323 K degrees for identifying the boronizing kinetics. Three distinct regions were identified on the surface of the specimens: Boronized layer, transition zone and matrix. This regions are shown in micrographs.

The optical and the SEM examinations revealed

that the boride layer formed on the surface of the specimens has a columnar morphology. Boride layer thicknesses of the specimens ranged from 12,3  $\mu\text{m}$  to 175,8  $\mu\text{m}$ .

The micro hardness measurements were carried out from the surface to the substrate by Vickers indenter with load 100 g. Boride layer hardness values changes between 952 – 2119 Hv.

The XRD analysis shown that the boronized layers mainly consisted of FeB and Fe<sub>2</sub>B. But as well as the

small amounts of different borides are formed such as  $Cr_2Ni_3B_6$  and  $Ni_2B$  in the layers. This situation can be explained by the high amount of Cr and Ni contents of the steel X5CrNi 18-10.

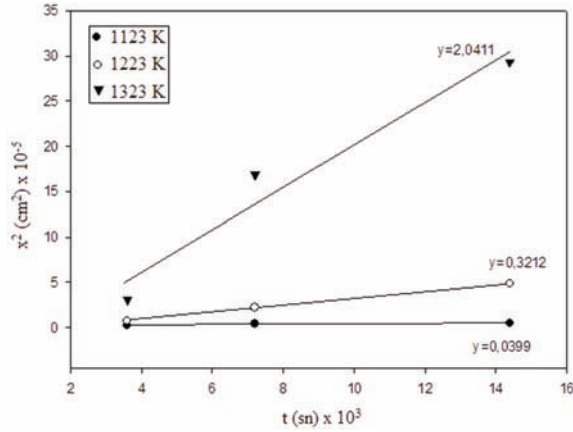


Figure 5. Square of the boride layer thicknesses on boronized steel X5CrNi 18-10 over treatment time

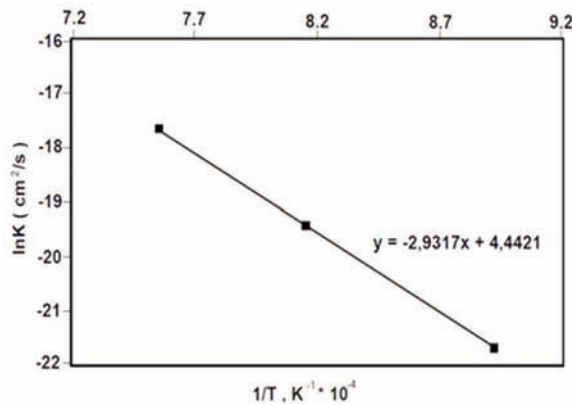


Figure 6. Growth rate constant vs. temperature of boronized steel X5CrNi 18-10

Table 5. The comparison of activation energy for diffusion of boron with respect to the different boronizing methods

Type of steel	Range of Temperature (K)	Boronizing Process	Activation Energy (kj/mol)	References
X5CrNi 18-10	1073-1223	Salt bath	253.35	Taktak (2006)[12]
X5CrNi 18-10	1123-1223	Powder pack	234.64	Kayalı (2013)[13]
X5CrNi 18-10	1023-1223	Plasma paste	123	Yoon et.(1999) [14]
X5CrNi 18-10	1123-1323	Powder pack	244	This study

For the calculation of boronizing kinetics used Arrhenius Equation and practical formulas.

As a result of calculations, activation energy of boronized X5CrNi18-10 steel has been determined as 244 kj/mol. This calculated value was compared with the literature. This comparisons can be seen in Table 5. Looking at the literature results, the activation energy value has been affected by boronizing methods rather than boronizing temperature.

### 5. Conclusion

The following informations have been obtained as the results of this study.

It is possible to develop useful non-oxide boride type layer on the surfaces of austenitic stainless steels by using Indirect Heated Fluidized Bed Furnace.

The microstructures of the boronized steels surfaces showed that three distinct regions such as boride layer, transition zone and matrix.

The boride layers formed on boronized steel have columnar morphology and the prolonged boronizing time and higher temperatures result in thicker boride layers.

The microhardness distribution of this layers were showed a gradient change. The measurements revealed that hardness values of the boride layers it can be concluded that the hardness was increased from the substrate to surface along. This is due to the amount of boron in the FeB phase is more than in that  $Fe_2B$  phase.

The XRD studies reveal that dominant phases are  $Fe_2B$  and FeB in the boronized layers. On the side since the amounts of Nickel and Chrome in X5CrNi 18-10 excessive  $Ni_2B$  and  $Cr_2Ni_3B_6$  phases were determined.

For the calculation of boronizing kinetics used Arrhenius Equation and practical formulas. According to the kinetic calculations performed by using layer thickness and boronizing time parameters are determined that the activation energy of boronized X5CrNi 18-10 stainless steel is 244 kj/mol.

### References

- [1] R. Beatty. The Element Boron, Marshall Cavendish Corp., 99 White Plains Road, Tarrytown, New York 10591,Printed in China (2005) 4.
- [2] R. Adair, Boron (Understanding the Elements of the Periodic Table), Rosen Publishing Group, 29 East 21st St. New York, NY 10010 (2007) 19.
- [3] DIN 17014-3: 1976-05 "Heat Treatment of Ferrous Materials; Notation to Indicate Heat Treatment Processes", English Version.
- [4] P. Topuz, E. Yılmaz, E. Gündoğdu, Materials Testing, 56(2) (2014) 104-110.
- [5] R.W. Reynoldson, Heat Treatment in Fluidized Bed

- Furnaces, The Materials Information Society, Materials Park, OH, ASM International, 1993.
- [6] İ. Özbek, C. Bindal, *Surface & Coatings Technology*, 154 (2002) 14-20.
- [7] B.S Mann, *Wear*, 208 (1997) 125–131.
- [8] R.X. Yan, X.M. Zhang, J.W. Xu, Z.G. Wu, Q.M. Song, *Materials Chemistry and Physics* 71 (1) (2001) 107–110.
- [9] J. Zuno-Silva, M. Ortiz-Domínguez, M. Keddamb, M. Elias-Espinosac, O. Damián-Mejía, E. Cardoso-Legorretac, M. Abreu-Quijanao, *Journal of Mining and Metallurgy Section. B-Metallurgy*, 50 (2) B (2014) 101 – 107.
- [10] AK. Sinha, Boriding (Boronizing), “ASM Handbook, Vol 4: Heat Treating”. Materials Park, OH: ASM International, (1991) 978-998.
- [11] O. Ozdemir, M.A. Omar, M. Usta, S. Zeytin, C. Bindal, A.H. Ucisik, *Vacuum*, 83 (2008) 175-179.
- [12] S. Taktak, *J. Mater. Science*, 41 (2006) 7590-7596.
- [13] Y. Kayalı, *The Physics of Metals and Metallography*, 114 (12) (2013) 1061-1068.
- [14] J.H. Yoon, Y.K. Jee, S.Y. Lee, *Surface and Coating Technology*, 112 (1999) 71-75.