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Investigation of Boronizing Kinetics of AISI 51100 Steel

M. Ipek, G. Celebi Efe, I. Ozbek, S. Zeytin, and C. Bindal

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In this study, some mechanical properties of borided AISI 51100 steel with high C concentration were investigated. Boronizing heat treatment was carried out in solid medium consisting of Ekabor-II at 850, 900, and 950 °C for 2, 4, 6, and 8 h. Morphology and mechanical properties of boride layer, and the effect of chemical composition on properties and kinetics of borides were investigated. The results of this study indicated that the morphology of the boride layer has a saw-tooth nature, and its hardness is over 1500 HV. Depending on process time and temperature, the depth of boride layer ranged from 30 to 106 µm. Optical and SEM studies and XRD analysis revealed that borides formed on the surface of steel substrates have dominantly single Fe_2B boride phase in addition to small amount of Cr_2B.

Keywords AISI 51100, boriding, Fe_2B, hardness, kinetics

1. Introduction

Boriding (or boronizing) is a promising thermochemical surface hardening treatment applied to many engineering components to improve their wear, oxidation, and corrosion resistance (Ref 1-3). The treatment has been applied to a wide range of materials including ferrous materials, non-ferrous materials, and some super alloys (Ref 2, 4). Boriding of ferrous materials is generally performed between 840 and 1050 °C. The process can be carried out in solid, liquid, or gaseous medium. At present, there are several boriding processes such as pack or paste boriding, liquid or molten salt boriding, electrochemical boriding, plasma-assisted boriding, available for the treatment of engineering components. The most frequently used method is pack boriding, a process similar to pack carburizing. The pack usually contains a source of boron, usually boron carbide (B_4C) or amorphous boron, an activator to deposit atomic boron at the work piece and diluents. Pack boriding involves embedding the component in the powder mix and sealing it in a container. The container is then heated up to the required temperature for the required time and cooled in air. The diffusion of B into steel results in formation of iron borides (FeB and Fe_2B) and the thickness of the boride layer is determined by the temperature and time of the treatment. Boriding of ferrous materials is a common practice and has been in use since the early 1900s (Ref 1). Due to their small size and high mobility, boron atoms diffuse into substrates, and some of them react with substrate atoms and form iron borides. Depending on the specific characteristics of the boriding process (such as type of powder mixture, temperature, time, and current density) and chemical composition of the base steel, a single or duplex layer may form, for instance, FeB and/or Fe_2B with low alloy steels. Dual-phase boride layers offer some tribological advantages due to a gradually declining hardness profile from the surface through the boride layer and well into the substrate. However, as seen in the examples of steel boriding, the higher boron content phase (FeB) on top may not be ideal for mechanical and tribological applications (Ref 1, 2). First of all, despite being very hard, the FeB top layer is very brittle and has a substantially different coefficient of thermal expansion. While cooling down after the boriding treatment, high tensile stresses develop in the FeB phase while compressive stresses form in Fe_2B; hence, borided steels with high FeB content develop extensive micro and macro cracks parallel to the borided surface layers. Additionally, the brittleness of FeB layers leads to severe flaking and spalling when a high normal or tangential load is applied. Consequently, a single Fe_2B boride layer is more desirable than a dual FeB-Fe_2B layer (Ref 5-12).

In this study, we developed a single-phase Fe_2B layer on AISI 51100 thrust roller or ball bearing steel substrates. This is original side of present study. The single Fe_2B phase was inspected by X-ray diffraction (XRD) and scanning electron microscopy (SEM) in backscattering mode. Additionally, Vickers microhardness examination was carried out to determine the hardness variation and the growth kinetics of the boriding layer was investigated.

2. Experimental Details

2.1 Substrate Material and Boronizing

The substrate material used for this study was AISI 51100 steel (Table 1). The test pieces had a rectangular shape, with dimensions of $15 \times 10 \times 10$ mm^3. Before boronizing heat treatment, all the samples were ground using 600 grid emery

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M. Ipek, G. Celebi Efe, I. Ozbek, S. Zeytin, and **C. Bindal**, Department of Metallurgy and Materials Engineering, Engineering Faculty, Sakarya University, Esentepe Campus, 54187 Sakarya, Turkey. Contact e-mail: mipek@sakarya.edu.tr.

papers to get surface finish. The hardness of the untreated AISI 51100 steel is 330 HVN. Boronizing heat treatment was carried out by pack boriding method using EKabor-II powders (B_4C, SiC, and KBF_4, etc.) as boron source. All samples to be boronized were packed in the powder mix and sealed in a stainless steel container. Boronizing was performed in an electrical resistance furnace under atmospheric pressure at 850, 900, and 950 °C for 2, 4, 6, and 8 h followed by cooling in air. Polished samples were etched with 3% nital before examinations.

2.2 Characterization

Microstructure analysis of borides formed on the test materials was performed with a JEOL JSM-6060 model SEM. The distribution of alloying elements in boride layer from surface to interior was determined by means of energy dispersive X-ray spectroscopy (EDS) analysis. The presence of borides formed in the coating layer was determined by XRD analysis. Rigaku X-ray diffractometer with a Cu Kα radiation source of a wavelength of 1.548 Å over a 2θ range from 10° to 90° was employed for the phase characterization of borided layer. The microhardness of borides was measured using a Leica microhardness tester under the loads of 50 g. The thickness of boride layer was measured via a digital instrument attached to optical microscopy.

Table 1 The chemical composition of substrate material (wt.%)

C	Si	Mn	P	S	Cr	Ni	Mo	Fe
0.921	0.296	0.741	0.0095	0.0111	0.944	0.0498	0.006	Balance

2.3 Kinetics

The kinetics of layer growth is controlled by perpendicular boron diffusion into the Fe_2B layer. According to Fick's law, the squared thickness of the boride layer as a function of boronizing time is described by Eq 1:

$$X^2 = Kt \qquad \text{(Eq 1)}$$

where X is the depth of boride layer (cm), t is the process time (s), K is the diffusion coefficient (cm^2/s) depending on boronizing temperature and is calculated from the slopes of the X^2 versus treatment time graphs. The relationship between diffusion coefficient D, temperature T, and activation energy Q, can be expressed by an Arrhenius-type equation as follows:

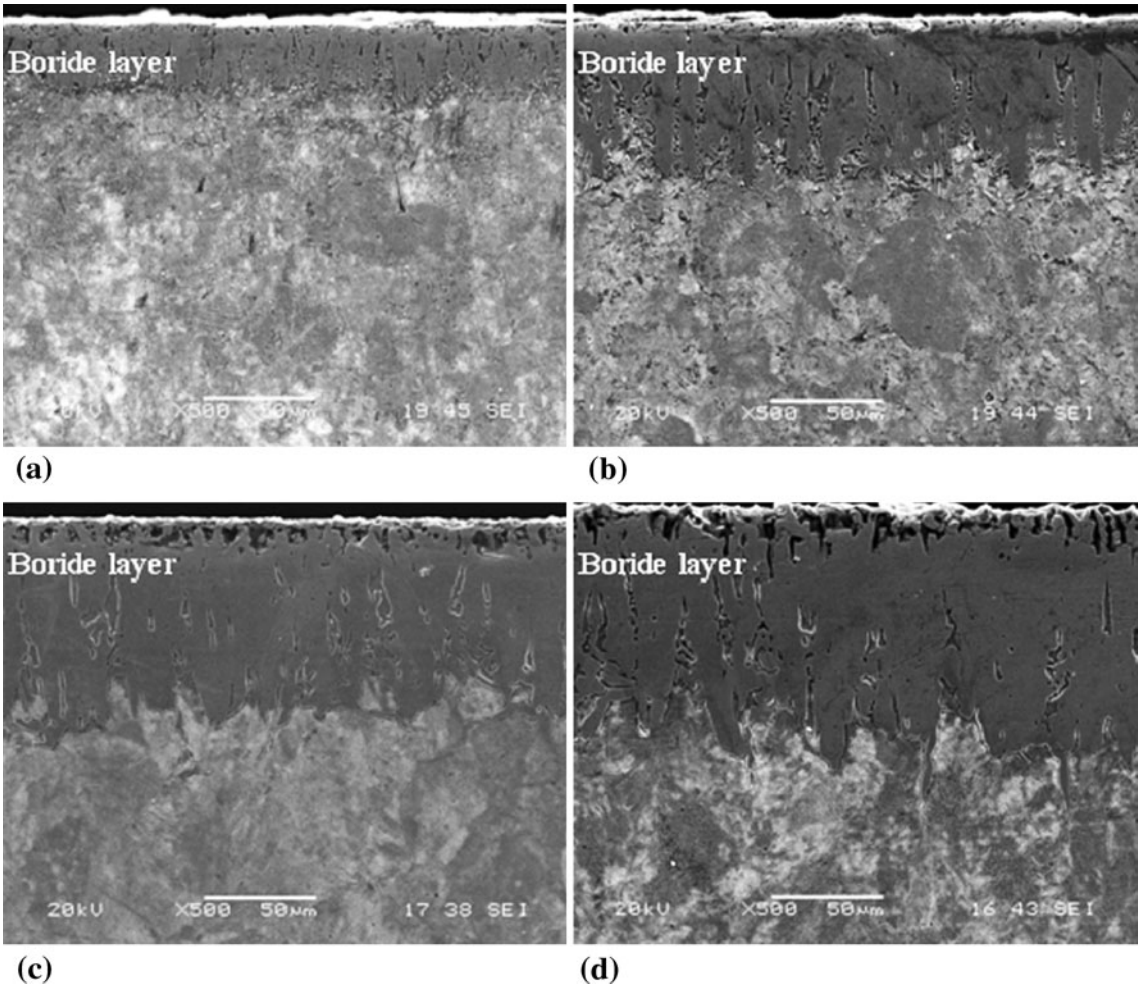


Fig. 1 SEM micrographs of borided steel at 850 °C for (a) 2 h, (b) 8 h and at 950 °C for (c) 2 h, (d) 8 h

$$K = K_o \exp(-Q/RT) \quad \text{(Eq 2)}$$

where K is diffusion coefficient, K_o is called the pre-exponential constant, Q is activation energy (J/mol) required to make the reaction occur, T is the absolute temperature (Kelvin), and R is the universal gas constant (J/mol/K) (Ref 13-15).

3. Results

3.1 Microstructure

Figure 1 shows SEM micrographs of dominantly borides having saw-tooth morphology which is required for good adhesion between the layer and the substrate. This morphology is a characteristics property of the boride layer and depends on the concentration of alloying elements as well as treatment temperature and time. Depending on the process time, temperature, and chemical composition of substrates, the depth of the boride layer ranged from 30 to 106 µm. The growth kinetics of the layer is analyzed by measuring the depth of boride layer as a function of the boronizing time and process temperature. It was found that there is nearly a parabolic relationship between thickness of borides and process time (Fig. 2). Boride layers increase in depth with increasing temperature and growth rate of boride layer decreases with increasing time. It is believed that with time, boron potential of boriding medium decreases.

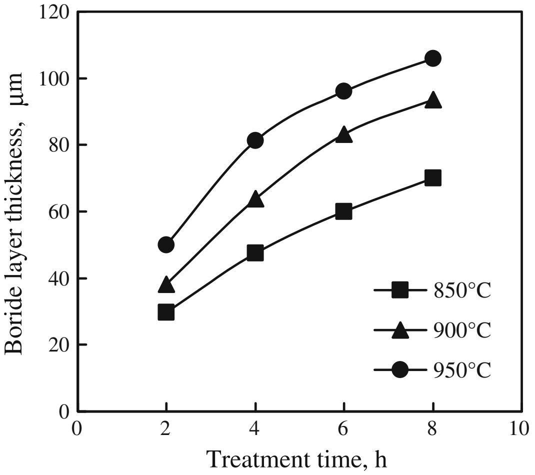


Fig. 2 The variation of the depth of boride layer as a function of process time

A single Fe_2B boride layer is more desirable than a dual FeB-Fe_2B layer, because FeB and Fe_2B phases have tensile and compressive residual stresses, respectively, causing cracking at interface of two borides. The preferred methods to prevent FeB growth are (i) diluting the boron concentration by pack boriding of powder mixtures, (ii) applying a much thinner boriding agent, or (iii) working at higher boriding temperatures for long enough to transform FeB into Fe_2B phase (Ref 5). Figure 3 gives SEM-BES micrographs of sample borided at 850 °C for 2 and 8 h. In this study, FeB boride was not observed even for lowest process temperature when treating for 2 and 8 h.

The distribution of alloying elements from surface to interior was determined by means of EDS. Figure 4 shows EDS dot analysis for determining the elements accumulated in the boride layer. It was found that iron and chromium have been dissolved in boride layer. Chromium is an element which forming chromium boride with high hardness. Also XRD studies confirm this result. XRD patterns of three samples borided at 850, 900, and 950 °C for 8 h are given in Fig. 5. As it can be seen, boride layer of each sample has dominantly Fe_2B boride phase, in addition to small amount of Cr_2B, moreover B_2O and SiC probably originated from boriding medium were detected.

3.2 Hardness

At present study, in general, single-phase boride layer was formed as a consequence of boronizing treatment. The variation of hardness of borides formed on the surface of AISI 51100 steel ranged from 1520 to 1800 HVN, whereas the hardness of the unborided steel substrate is 330 HVN. The microhardness values of the samples are enhanced by increasing boriding time and the temperature (Fig. 6). These results are in good agreement with the nature of boronizing process because of more boron atoms diffused into the surface with the increasing time and diffusion of boron atoms slightly increased with increment in the temperature. As a result of this, more boron compounds such as Cr_2B formed in the borides layer and the hardness increased. The distribution of hardness from surface to interior of AISI 51100 bearing steel borided at 950 °C for 8 h is

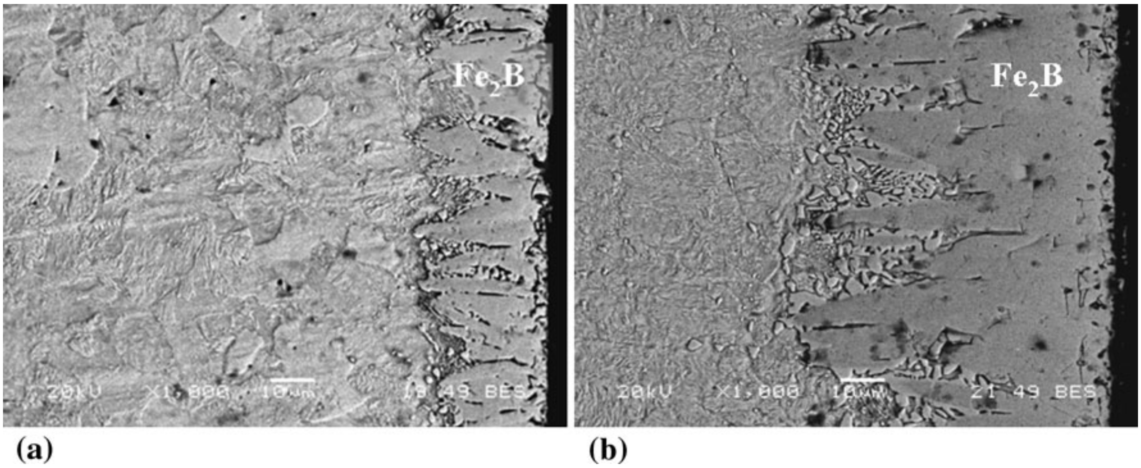
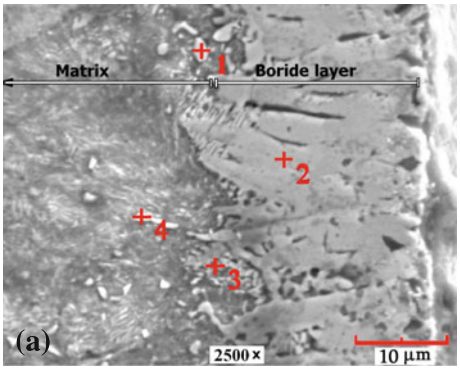


Fig. 3 SEM-BES micrograhs of sample borided at 850 °C (a) 2 h and (b) 8 h



wt.%	Mark			
	1	2	3	4
C	4.7		11.2	7.8
Si				0.6
Cr	1.3	0.8	1.0	1.0
Fe	94.0	99.2	87.8	90.6

(b)

Fig. 4 (a) SEM micrograph and (b) EDS dot analysis of sample borided at 850 °C for 2 h

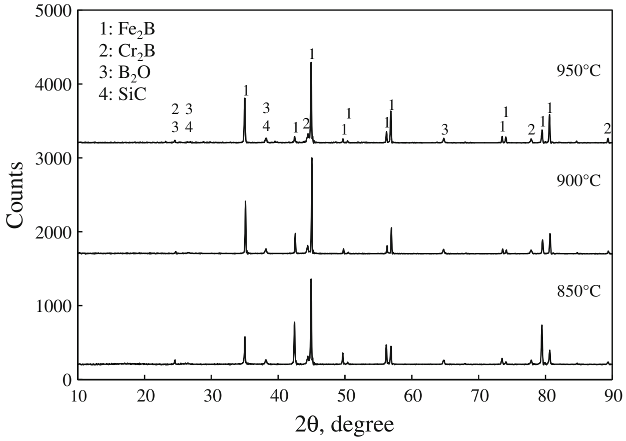


Fig. 5 XRD patterns of AISI 51100 steel borided at different temperatures for 8 h

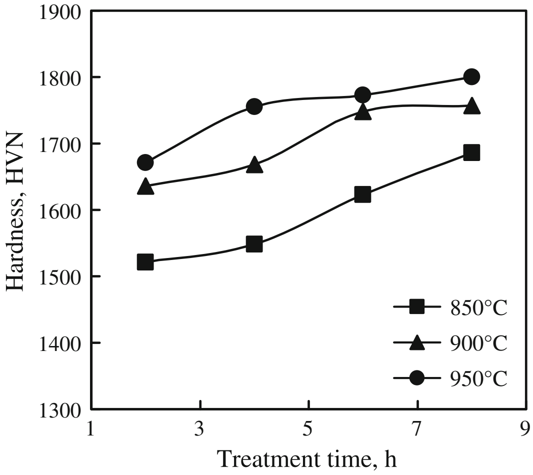


Fig. 6 The hardness variation of borided samples with process temperature and time

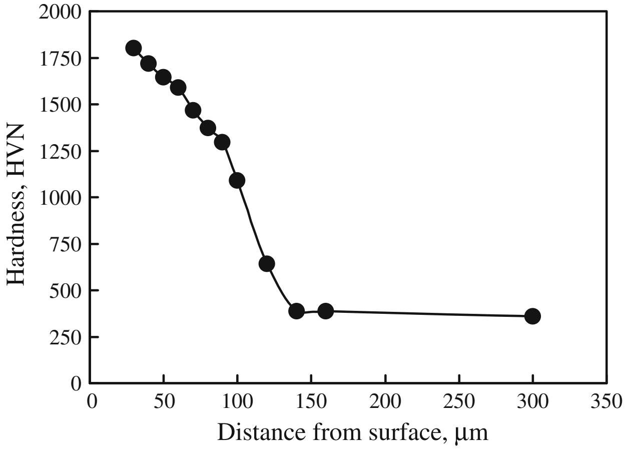


Fig. 7 The hardness profile of sample borided at 950 °C for 8 h

shown in Fig. 7. As it can be seen, the hardness of boride layer is much higher than that of substrate. There is a gradually decrease in hardness from surface to interior.

3.3 Kinetic Studies

In this study, the effects of the boriding time and temperature on the growth kinetics of the boriding layer were investigated. Primarily, from the data of layer depth of borided AISI 51100 steel, diffusion coefficient values were calculated using Eq 1 (Fig. 8). The calculated diffusion coefficient values are given in Table 2.

The plot of ln D versus $1/T$ reveals a linear relationship (Fig. 9) and activation energy of 106 kJ/mol was measured from the slope of the straight line for AISI 51100 steel.

4. Discussion

SEM cross sectional examinations revealed that borides formed on the surface of AISI 51100 bearing steel is of saw-tooth morphology providing good adhesion with substrate. As it is known well, during boronizing, the alloying elements in the steel undergo redistribution due to diffusion phenomenon. This distribution depends on the solubility of each element in solid phase, as well as on the process temperature. Thus, the properties of base steel and surface coating are significantly modified by these alloying elements. The higher the process temperature and the longer the treatment time, the thicker the boride layer became on the borided steel samples. Depending on process temperature and time, the depth of boride layer ranged from 30 to 106 µm. The presence of boride phases on the surfaces of borided steels was determined by XRD analysis.

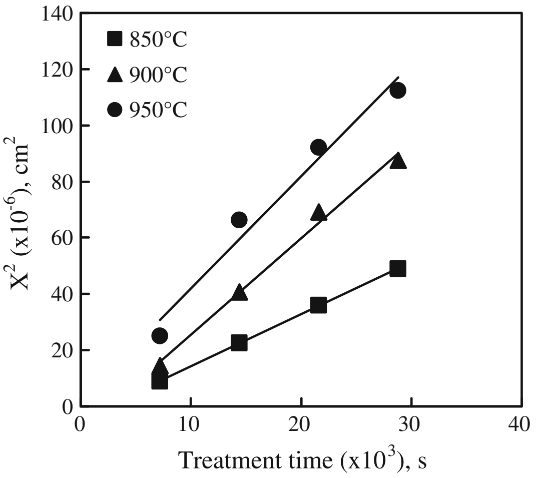


Fig. 8 Square of the boride layer thickness of borided steel as a function of process time

Table 2 Diffusion coefficient values of samples borided at different temperature

Boriding temperature, °C	Diffusion coefficient, cm^2/s
850	1.9×10^{-9}
900	3.4×10^{-9}
950	4.0×10^{-9}

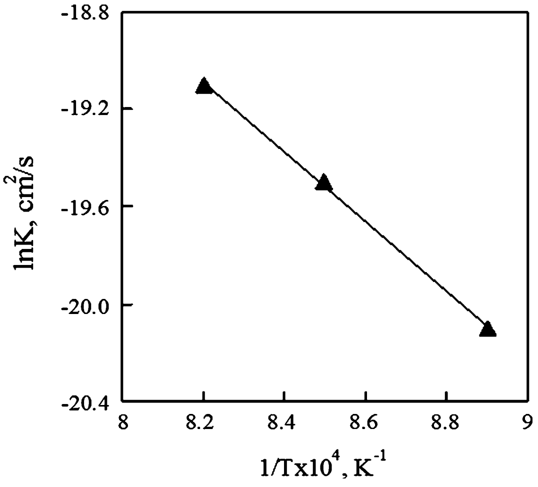


Fig. 9 ln K versus $1/T$

They showed that the dominant phases formed in coating layer are Fe_2B and Cr_2B. In the present study, formation of single boride layer is an important advantage. Double boride layers were obtained by plasma boriding method in work done on similar steel (Ref 16). FeB was not detected by XRD analysis and same phase was not observed SEM micrographs. The reason for this is probably low boron concentration of boriding medium. It was found that the hardness of borides is much higher than that of substrate. The growth rate of boride layer is controlled by boron diffusion in the Fe_2B layer and layer growth occurs as a consequence of boron diffusion perpendicular to the surface of the specimen. The plots of growth rate constant against reciprocal process temperature reveal a linear relationship. Growth kinetics of the borided layer was analyzed by measuring the extent of penetration of the Fe_2B layer as a function of boronizing time and temperature. It was observed that the higher the process temperature, the higher the growth rate becomes. This is characteristic of diffusion-controlled process. EDS analysis revealed that carbon and silicon are not soluble in the boride layer, and carbon and silicon are effectively pushed from the surface to the interior by boron atoms. EDS analysis verified that silicon is concentrated beneath the boride layer as expected. Chromium was dissolved in the coating layer and formed Cr_2B. At the present study a 106 kJ/mol activation energy was determined for AISI 51100 bearing steel.

5. Conclusion

The following results may be drawn from the present study.

(1) Boride layers formed on AISI 51100 steel have a saw-tooth morphology.
(2) Boride layers have a desirable single Fe_2B boride phase.
(3) Hardness of boride layers is approximately 1800 HVN, and hardness of substrate after boriding process is 380 HVN.
(4) Boriding activation energy for AISI 51100 steel is 106 kJ/mol.

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