Microstructural alteration and oxidation behavior of boronized stainless steel AISI 440C after heat treatments

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Original Article

Abstract

The martensitic stainless steel AISI 440C was boronized at a temperature of 950 °C for about 4 hr. Heat treatments at a temperature of 850 °C for about 2–8 hr were performed to eliminate the FeB phase of the boride layer. The oxidation investigations were carried out at a given temperature of 900 °C on different surface conditions. It was found that the FeB phase was completely dissolved and transformed to the Fe2B phase after a heat treatment at a temperature of 850 °C for about 8 hr. The oxidation behavior of the non-boronized, boronized and boronized with heat treatment of 8 hr conditions exhibit a parabolic manner, while the specimens boronized with heat treatments of 2 – 6 hr show a linear manner. The single-phase (Fe2B) boride layer on the martensitic stainless steel AISI 440C possesses a lowest oxidation rate as compared to other investigated surface conditions.

Keywords: oxidation resistance, thermochemical surface treatment, heat treatment, martensitic stainless steel, boronizing

1. Introduction

Stainless steel is one of the most widely used engineering materials. It has excellent mechanical strength and good corrosion resistance especially martensitic stainless steels (Davis, 2000). In recent years, not only the complicated and high-loading applications but also high-temperature applications are much more required. Therefore, to enhance a service lifetime, various surface treatments are mentioned for improving wear resistance and oxidation resistance of stainless steels. A boronizing process is a thermochemical surface treatment which provides a boride layer with outstanding properties, i.e., wear, oxidation and corrosion resistances and can be applied on various metallic materials (Atik, Yunke, & Merç, 2003; Davis, 2002; Lee, Kim, & Kim, 2004; Sen, Sen, & Bindal, 2006; Sinha, 1991). Actually, the main purpose of boronizing process is to improve the wear resistance of various metallic materials. However, other advantageous properties of the boride layers such as high-temperature oxidation resistance and high corrosion resistance were investigated and reported by several researchers (Davis, 2002; Jaques, & Butt, 2015; Kartal, Timur, Sista, Eryilmaz, & Erdemir, 2011; Li, Dai, Cheng, Wang, & Huang, 2012; Santhanakrishnan, Kong, & Kovacevic, 2011; Sinha, 1991). The boride layer formed on high alloying steels is usually a double-phase (FeB and Fe2B) type. The boron-rich phase, FeB is more brittle than Fe2B phase and shall be eliminated before use. The conventional heat treatment is a simple method to diminish FeB phase on the double-phase boride layer. The diffusion and phase transformation concepts were used to explain this phenomenon (Davis, 2002; Kartal, Timur, Sista, Eryilmaz, & Erdemir, 2011; Sinha, 1991). During heat treatment as well as phase transformation, the oxidation resistance of the double-phase boride layer shall be altered and is of a particular interest. Therefore, in this paper, the microstructural alteration and oxidation behavior of the boronized stainless steel AISI 440C after heat treatments were addressed and clarified. The microstructural alteration was characterized using an optical microscope and X-ray diffraction technique (XRD). The oxidation rate of the boronized with and without heat treatments were calculated and compared to the non-boronized martensitic stainless steel AISI 440C.
2. Materials and Experimental Procedures

The investigated materials is a martensitic stainless steel AISI 440C. The chemical compositions are 1.04% C, 0.38% Mn, 0.41% Si, 0.021% P, 0.001% S, 16.59% Cr and 0.43% Mo (all values in wt.%). A cylindrical shape of samples was 13 mm in a diameter and 10 mm in a length. Before boronizing process, all samples were ground up to 600 grit SiC paper for a clean and good surface. The boronizing process was carried out in a solid medium consisting of Ekabor-I powders from BorTec GmbH, Germany. The samples were placed with a distance of 15 mm and packed as well as buried in Ekabor-I powders into a steel container with a lid and cement seal. The steel container was heated in electric furnace under argon atmosphere at a temperature of 950 °C for a boronizing time of 4 hr and then cooled in air to room temperature. After boronizing process, some boronized specimens were heated at a given temperature of 850 °C with soaking times of 2, 4, 6 and 8 hr under argon atmosphere and finally cooled in air to room temperature. Microstructures and kind of the formed, as well as altered layers, were characterized using an optical microscope and XRD technique with Cu Kα radiation source (λ=0.154 nm), respectively. The thickness values of the formed layer were measured using an optical microscope with an image analyzer program. The hardness depth profile was measured using a Vicker microhardness tester with a load of 50 g. The oxidation tests were conducted in an electric furnace at a temperature of 900 °C with total time of 50 hr. The boronized specimens of both with and without heat treatment process were taken out of the furnace and cooled to room temperature at various intervals for mass measurement using an electronic analytical balance with a sensitivity of 0.01 mg. The total mass of a specimen together with the crucible was recorded.

3. Results

3.1 Microstructure and characterization

After the boronizing process at a temperature of 950 °C for about 4 hr, a double-phase boride layer with a thickness about 41 µm was detected. The cross-sectional microstructure of the boride layer is shown in Figure 1. The boride layer on the martensitic stainless steel AISI 440C has smooth and more compact morphology as compared to low or unalloyed steels (Atık, Yunker, & Merić, 2003; Campos-Silva et al., 2010; Campos, Palomar, Amador, Ganem, & Martinez, 2006; Lee, Kim, & Kim, 2004; Rie & Broszeit, 1995; Taktak, 2006). The outer dark phase of the boride layer in Figure 1 is the FeB phase with 16.23 wt.% B. The brighter phase is Fe3B with 8.83 wt.% B (Davis, 2002; Sinha, 1991). The XRD spectrums in Figure 5 are used to confirm the phases of the formed boride layer as illustrated in Figure 2. The XRD patterns can confirm that the phases of the formed boride layer are FeB and Fe3B which are related to the microstructure in Figure 1. Additionally, the near surface hardness of the boride layer could be reached about 2000 HV, whereas the hardness of the substrate of approximately 600 HV was measured. The hardness depth profile of the martensitic stainless steel AISI 440C boronized at 950 °C for about 4 hr was measured and shown in Figure 3.

The double-phase boride layer is still observed after heat treatment for about 2 – 6 hr. However, the FeB phase thickness decreases with the soaking time increases till 6 hr as illustrated in Figure 4a-c. Finally, only single-phase Fe2B boride layer of about 53 µm is detected after heat treatment for about 8 hr (Figure 4d). The XRD patterns in Figure 5 are used to confirm above mention. The altered thickness values of the FeB and Fe2B with different heat treatment conditions are given in Figure 6.

3.2 High-temperature oxidation behavior

After the boronizing, the high-temperature oxidation tests were performed at a given temperature of 900 °C for a total time of 50 hr. Two characteristics of the oxidation behavior are detected. First, the parabolic manner was observed for three conditions, e.g., non-boronized, boronized and boronized with heat treatment for about 8 hr as shown in Figure 7a. For the
Figure 4. Cross-sectional microstructure of the boronized martensitic stainless steel AISI 440C after heat treatment at a temperatures of 850 °C for (a) 2 hr, (b) 4 hr, (c) 6 hr and (d) 8 hr.

Figure 5. XRD patterns of various surface of the boronized martensitic stainless steel AISI 440C; (a) without heat treatment, with heat treatment at a temperature of 850 °C for (b) 2 hr, (c) 4 hr, (d) 6 hr and (e) 8 hr.

Figure 6. Alteration of the FeB and Fe2B thickness during heat treatments at a temperature of 850 °C.

parabolic manner, the squared weight grain of the oxidized sample as a function of time can be described in Equation (1) as follows (Fontana, 1986):

\[ m^2 = k_p t + c \]  

(1)

where \( m \) is the weight gain per unit area (mg/cm²), \( t \) is the oxidation time (hr), \( c \) is a constant, \( k_p \) is the oxidation rate at a constant oxidation temperature. Second, the linear manner was seen for other conditions, e.g., boronized with heat treatment for about 2, 4 and 6 hr as illustrated in Figure 7b. For linear manner, the weight gain of the oxidized sample as a function of time can be described in Equation (2) as follows (Fontana, 1986):

\[ m = k_l t \]  

(2)

where \( m \) is the weight gain per unit area (mg/cm²), \( t \) is the oxidation time (hr), \( k_l \) is the oxidation rate at a constant oxidation temperature. After oxidation test at a temperature of 900 °C for about 50 hr, XRD was performed to verify the oxidized surfaces as shown in Figure 8. The iron oxide, Fe₂O₃ pattern is observed in all conditions after the high-temperature oxidation tests.

Figure 7. Evolution of the weight gains over soaking time during the oxidation tests of the various surface conditions; (a) non-boronized, boronized, boronized with heat treatment of 8 hr, (b) boronized with heat treatment of 2, 4 and 6 hr.
the formed boride layers on the martensitic stainless steel AISI 440C have smooth and more compact morphology due to high alloying elements. The development of a jagged boride/substrate interface is suppressed in consequence of an increase of alloying elements and carbon content of the substrate (Davis, 2002; Sinha, 1991). Alloying elements in the martensitic stainless steel AISI 440C affected the diffusion of boron atoms into the steel, as a consequence of a smooth boride/substrate interface and double-phase boride layer (Figure 1). The double-phase boride layer is affected by applied heat treatment at a temperature of 850 °C. The phase transformation was observed due to the chemical concentration gradient between the FeB (16.23 wt.% B) and FeB (8.83 wt.% B) phases, and then a diffusion process occurred. The boron atoms can diffuse from high chemical potential side to low chemical potential side at the interface in the boride layer and steel substrate during the heat treatment process at a high temperature (Davis, 2002; Kartal, Timur, Sista, Eryilmaz, & Erdemir, 2011; Naemchanthara & Juijerm, submitted; Sinha, 1991). Thus, the FeB phase was slowly dissolved at the FeB and FeB interface during the heat treatment in argon atmosphere determined by Equation (3). Afterwards, the FeB phase increased at the interface of the FeB and Fe (substrate) determined by Equation (4) (Figure 4 and 6) (Naemchanthara & Juijerm, submitted). Finally, the double-phase boride layer was changed entirely to the single-phase boride layer by heat treatment at a temperature of 850 °C for 8 hr (Figure 4 and 5) (Davis, 2002; Kartal, Timur, Sista, Eryilmaz, & Erdemir, 2011; Sinha, 1991).

\[ 2\text{FeB} \rightarrow \text{Fe}_2\text{B} + \text{B} \]  

\[ 2\text{Fe} + \text{B} \rightarrow \text{Fe}_2\text{B} \]  

4. Discussion

After boronizing process at a temperature of 950 °C for 4 hr, the formed boride layers on the martensitic stainless steel AISI 440C have smooth and more compact morphology due to high alloying elements. The developed boride/substrate interface is suppressed in consequence of an increase of alloying elements and carbon content of the substrate (Davis, 2002; Sinha, 1991). Alloying elements in the martensitic stainless steel AISI 440C affected the diffusion of boron atoms into the steel, as a consequence of a smooth boride/substrate interface and double-phase boride layer (Figure 1). The double-phase boride layer is affected by applied heat treatment at a temperature of 850 °C. The phase transformation was observed due to the chemical concentration gradient between the FeB (16.23 wt.% B) and FeB (8.83 wt.% B) phases, and then a diffusion process occurred. The boron atoms can diffuse from high chemical potential side to low chemical potential side at the interface in the boride layer and steel substrate during the heat treatment process at a high temperature (Davis, 2002; Kartal, Timur, Sista, Eryilmaz, & Erdemir, 2011; Naemchanthara & Juijerm, submitted; Sinha, 1991). Thus, the FeB phase was slowly dissolved at the FeB and FeB interface during the heat treatment in argon atmosphere determined by Equation (3). Afterwards, the FeB phase increased at the interface of the FeB and Fe (substrate) determined by Equation (4) (Figure 4 and 6) (Naemchanthara & Juijerm, submitted). Finally, the double-phase boride layer was changed entirely to the single-phase boride layer by heat treatment at a temperature of 850 °C for 8 hr (Figure 4 and 5) (Davis, 2002; Kartal, Timur, Sista, Eryilmaz, & Erdemir, 2011; Sinha, 1991).
layer formed during the heat treatment process. At the microcracks, there are a preferred diffusion path for oxygen atoms from environment into the boride layer. The oxidation rate could be probably enhanced by local stresses at the microcracks. Consequently, a linear characteristic was observed for the oxidation rates (Fontana, 1986; Trethewey, & Chamberlain, 1995). By fitting the measured data, the oxidation rates of the boronized specimens with heat treatment of 2, 4 and 6 hr, the oxidation rates of 0.00028, 0.00020 and 0.00013 mg cm\(^{-2}\) hr\(^{-1}\) were determined, respectively. The oxidation test of the boronized condition illustrates that the FeB phase exhibits a high and parabolic oxidation rate (Figure 7a). If the FeB phase decreases with existed microcracks after heat treatment process, a lower oxidation rate with linear manner. The hardness values of the boronized condition illustrate that the FeB phase decreases with increasing soaking time. For about 8 hr at a temperature of 850 °C, the FeB phase was completely dissolved and transformed to the Fe\(_2\)B phase (single-phase boride layer) on the martensitic stainless steel AISI 440C.


