Effect of boronizing on the cyclic oxidation of stainless steel

E. Dokumaci [a], I. Özkan [b],*, B. Önay [a]

[a] Faculty of Engineering, Metallurgical and Materials Engineering Department, Dokuz Eylül University, Izmir, Turkey
[b] Torbali Vocational School, Dokuz Eylül University, Izmir, Turkey

A R T I C L E   I N F O

A B S T R A C T

In this study, the effect of boronizing surface treatment on the cyclic oxidation behavior of 304-type stainless steel was investigated. Boronizing treatment was carried out at 950 °C for 4 and 8 h. XRD analyses indicated FeB, Fe_2B, and CrB phases as the boronizing products formed in the steel. During the cyclic oxidation tests conducted at 800 °C in air, boronized samples gained less weight than as-received samples and had oxide scales that grew according to the parabolic law. Such kinetic behavior is thought to be related to the presence, besides metal oxides, of an iron borate ($FeBO_3$) and a liquid (B_2O_3) phase in the scale. Based on the analyses results and the observation that alloy samples that were boronized the longest had the lowest weight gains during oxidation, it is proposed that the boronizing surface treatment can be more effective under cyclic oxidation conditions because the complete conversion of borides to oxides may take longer as a result of thermal cycling.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Boronizing is a thermochemical surface treatment by which boron atoms diffuse into metallic materials, for predetermined times, to form stable borides of some or all the elements in the metal. This process has been used, mostly, to improve tribological properties of ferrous as well as some non-ferrous materials [1,2]. The application of this process to metallic materials with the purpose of increasing their aqueous corrosion resistance has also been reported [3,4]. Recently, borides of metals like Ti and Zr have been shown to have good high temperature oxidation resistance because of both the refractory nature of their oxides and the formation of a liquid oxidation product [5]. Such borides are named "ultra-high temperature materials" and are being considered for use in future supersonic aircraft.

The authors have done work on the oxidation behavior of some boron compounds at high temperatures, and they have been investigating the effect of boronizing on the oxidation behavior of high temperature materials [6,7]. Here, they have studied the effect of boronizing on the cyclic oxidation behavior of the AISI 304-type stainless steel. Although this steel has numerous applications in industrial machinery and processes, its use is limited to about 870 °C under intermittent conditions in air because its Cr and Ni contents are lower than those of the 309 and 310-type steels, which are generally utilized at such temperatures [8]. The purpose of this study is to investigate whether boronizing can improve the oxidation resistance of this steel under working conditions, which involve thermal cycling. Even though the number of studies related to the effect of boron surface treatment on metal oxidation is increasing, only a few of them have been conducted under cyclic conditions [9–11].

2. Materials and Methods

AISI 304-type steel samples measuring $15 \times 15 \times 1.5$ mm were cut from plates and their surfaces were cleaned first, with 400 and 800 grade emery papers, then with acetone ultrasonically. Samples in this condition are referred as "as-received" in the text below.

The source of boron for the boronizing treatment was the commercial (Ekabor®2) powder. As-received samples were covered with this powder inside a metallic container. To start the treatment, the container was placed inside a box furnace that had been preheated to 950 °C. Two boronizing tests lasting for 4 and 8 h were conducted by using five separate samples in each test. After boronizing, one of the samples in each group was used for characterization by a scanning electron microscope (SEM; JEOL-JSM 6060) equipped with an energy dispersive spectrometer (EDS; IXRF System 500) and an x-ray diffractometer (XRD; Rigaku D/Max-2200/PC) to determine the nature and structure of the boride zones developed in the samples. Later, the two groups of boronized samples and four "as-received" samples were oxidized at 800 °C, in air, for a total of 20 h in 4 cycles each lasting 5 h. After each thermal cycle, samples were cooled to room temperature and their weight changes were recorded. SEM/EDS and XRD analyses were also conducted on the oxidized samples.

3. Results and Discussion

The results of the XRD analysis conducted on the steel sample boronized for 8 h are shown in Fig. 1. Most of the x-ray peaks were

* Corresponding author. Tel.: +90 232 8531828 145; fax: +90 232 8531606.
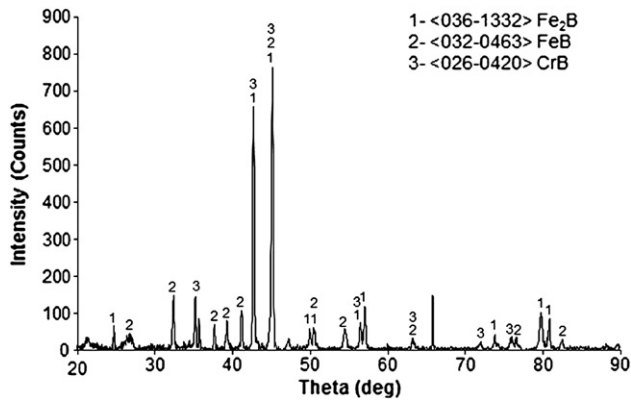E-mail address: ilker.ozkan@deu.edu.tr (I. Özkan).

Fig. 1. XRD analysis results for the 304 steel samples after boronizing at 950 °C for 8 h.

Fig. 3. Change in the boride layer thickness with boronizing time for 304 samples.

of the Fe_2B and FeB phases. A few peaks in the XRD data suggested also the presence of the CrB phase. Although the steel contains about 8 w/o Ni, borides of this element were not observed. This was possible due to the relatively lower thermodynamic stability of nickel borides [12]. Also, because the analysis was conducted on the near-surface regions of the sample, boride phases of the alloying elements which developed in the inner parts of the sample might not have been detected.

In Fig. 2, a cross-sectional view of the sample that was boronized for 8 h is shown. Three different zones are visible in this SEM picture obtained in the BE (back-scattered electron) mode. It is thought that as boron diffused from the "pack" into the steel substrate, it reacted with iron as well as chromium to form the Fe-rich Fe_2B phase in the sample. As this boride layer thickened and the diffusion rate of boron decreased, the Fe_2B phase transformed to FeB by reacting with more boron, thus forming a zone of this higher boride in the outer regions of the samples. Upon precipitation deeper in the metal, the Fe_2B phase formed a second zone underneath the FeB zone. Since the contrast in the SEM/BE mode arises from the differences among the atomic numbers of the elements, darker appearances of these zones indicated the presence of boron-rich products inside them.

Beyond the Fe_2B layer, another zone generally referred as the "diffusion zone" was present. Darker appearances of the grain boundaries and interiors, in this zone, suggested that formation of Fe_2B and, possibly, borides of the alloying elements continued in the alloy matrix. The observed decoration of the grain boundaries indicated that such fast-diffusion paths were favored by the boron atoms during the boronizing process.
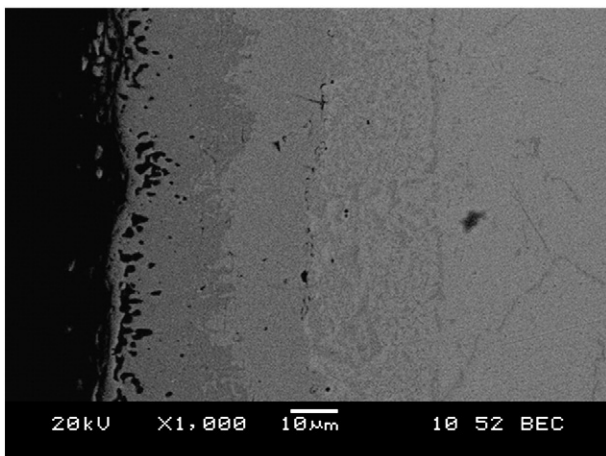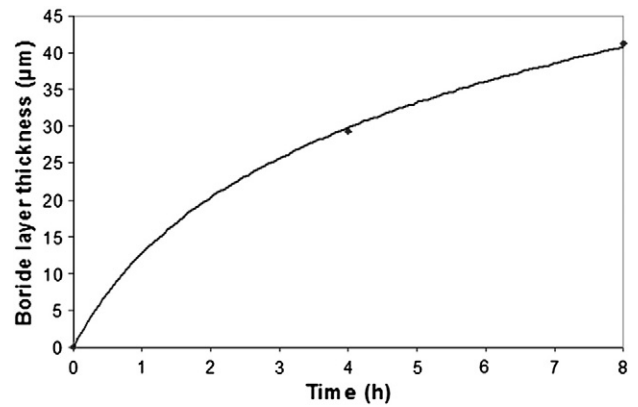
In accordance with the other studies reported in the literature [4,11,13], the interface between the boride zone and the diffusion zone was smooth, as seen in Fig. 2, unlike the case for carbon steels in which "needle-like" interfaces develop [1,2,9]. It has been suggested that the high alloy content of this type of steel decreases the diffusion rate of boron atoms causing the formation of a smooth boride/metal interface [14–16]. The dependence of the boride layer thickness on the test duration is shown in Fig. 3. Thicknesses of the total boride zones were 29 and 41 μm after 4 and 8 h of boronizing at 950 °C, respectively.

Results of the cyclic oxidation tests conducted at 800 °C, in air, on the boronized samples and as-received samples are shown in Fig. 4. All samples gained weight during almost all the cycles conducted. However, weight gains of the as-received sample were relatively higher. Furthermore, samples which were boronized the longest had the lowest weight gain at the end of each cycle. Although some spallation of oxidation products were observed from the samples during these tests, their amount was not significant compared to the amount of weight gains measured. In Fig. 5, squared values of the sample weight changes shown in Fig. 4 are plotted against the oxidation time. Linear nature of the lines connecting the data points of the boronized samples clearly indicated that oxide scales over the boronized samples grew in accordance to the parabolic law [17]. A similar kinetic behavior, however, was not observed for the as-received samples.

XRD analysis of the oxide scale formed over one of the 304 alloy samples boronized for 8 h showed that iron oxides (Fe_2O_3, $FeCr_2O_4$, Fe_3O_4), iron borate; $FeBO_3$ and Cr_2O_3 formed as the oxidation products upon exposure of the sample, to air, at 800 °C (Fig. 7). SEM/ EDS analyses conducted across the oxide scale (Fig. 6) indicated high Cr concentrations in the outer parts of the scale (Table 1), supporting the XRD results above. Although boron oxide (B_2O_3) was

Fig. 2. SEM photograph of the cross section of the 304 steel samples boronized at 950 °C for 8 h.

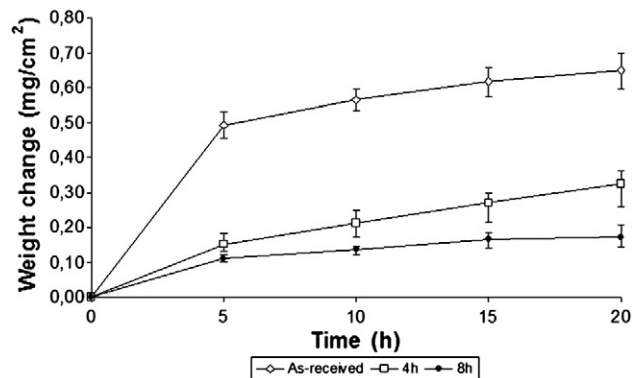Fig. 4. Oxidation weight changes, with error bars, measured for as-received samples and boronized samples.