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Corrosion Behavior and Microstructure of Borided Tool Steel

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ABSTRACT

In the present study, the corrosion behaviors of borides formed on cold work tool steel have been investigated in a 4% M HCl acid solution. Boriding was performed in a solid medium consisting of Ekabor-II powders at 850 and 950°C for 6 h. The boride layer was characterized by SEM, EDS, XRD and the hardness tester. XRD analysis of boride layers on the surface of the samples revealed the existence of FeB, Fe2B, CrB, Cr2B and MoB compounds. Depending on the chemical composition of substrates and boriding time, the boride layer thickness on the surface of the steel ranged from 13.14 µm and 120.82 µm. The hardness of the boride compounds formed on the surface of the samples ranged from 1806 to 2342 HV0,05, whereas Vickers hardness values of the untreated the samples was 428 HV0,05. The corrosion resistance of the borided steels was higher compared with that of the unborided steels. The borided steels increased the corrosion resistances of the steels 8–17- fold.

Keywords: Cold work tool steel, Boriding, Micro-hardness, Corrosion.

1. INTRODUCTION

Cold work tool steels have high chromium content and are commonly used engineering materials. Therefore, there has been extensive research on the development of surface treatment processes to improve the corrosion, wear and oxidation resistance of the cold work tool steels for high-temperature and high-pressure applications in recent years [1-7].

Boriding is a thermomechanical surface-hardening process, in which boron atoms are diffused into the surface of a workpiece to form borides with the base materials. Thus, the boriding process enhances the corrosion and wear resistance of metallic and non-metallic surfaces covered with boride layers [8,9]. Thermal diffusion treatments of boron compounds used to form iron borides typically require process temperatures of 700-1000 °C. The process can be carried out in solid, liquid, gaseous or plasma medium [10-13].

The corrosion of borided steels has not yet been explored extensively; only a few studies have been reported [14-17]. Also, there is no information about the corrosion behavior of borided cold work tool steels. The main objective of this study was to investigate the characterization and corrosion behaviors of borided cold work tool steel in a 4% M HCl acid solution. Structural and corrosion properties were investigated using optical microscopy, XRD, SEM, EDS, microhardness tests.

2. METHODS

The high alloy cold work tool steel essentially contained 0.90 wt.% C, 0.50 wt.% Mn, 7.80 wt.% Cr, 2.50 wt.% Mo and 0.50 wt.% V. The samples were cylindrical with a diameter of 25 mm and thickness of 8 mm. Boriding heat treatment was carried out by using a solid boriding method with commercial Ekabor-II powders. All samples to be borided were packed in the powder mix and sealed in a stainless steel container. Boronizing heat treatment was performed in an electrical resistance furnace under atmospheric pressure at 850 and 950ºC for 6 h followed by cooling in air.

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The microstructures of polished and etched cross-sections of the specimens were observed under a Nikon MA100 optical microscope. The presence of borides formed in the coating layer was confirmed by means of X-ray diffraction equipment (Shimadzu XRD 6000) using Cu Kα radiation. The hardness of the boride layers was measured on the cross-sections by means of Shimadzu HMV-2 Vickers indenter with 50 g loads.

The acid solution used was 4% M HCl. The aforementioned cylindrical borided steels and untreated steels were weighted before immersion, with an accuracy of 0.01 mg. At specific time intervals the specimens were withdrawn from the solutions and weighted without any additional treatment. Thus, the weight loss in relation to the initially exposed surface was continuously recorded. The immersion tests were repeated 19 times and mean values were used for the acquisition of weight loss curves. Before and after each corrosion test, each sample was cleaned with alcohol. Corrosion surfaces were investigated by SEM and EDS (Leo 1430 VP) analysis.

3. RESULTS

The cross-sections of the optical micrographs of the borided cold work tool steel at the temperature of 850 and 950ºC for 6 h are shown in Figure 1a and 1b.

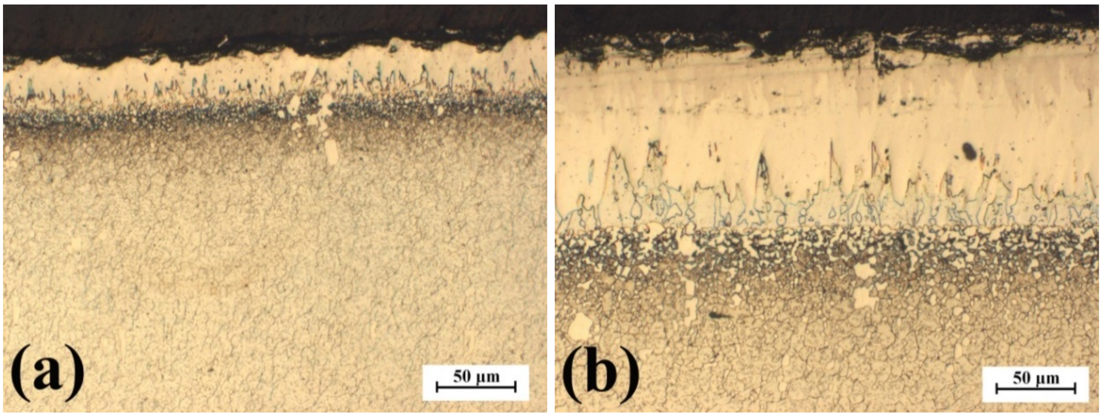

Figure 1: The cross-section of the borided cold work tool steel: a) 850ºC-6h, b) 950ºC-6h.

As can be seen, the borides formed on the cold work tool steel substrate have a smooth morphology due to higher alloy content. It was found that the coating/matrix interface and matrix could be significantly distinguished and the boride layer had a columnar structure (Figure 1). Depending on the chemical composition of substrates and boriding time, the boride layer thickness on the surface of the steel ranged from 13.14 µm and 120.82 µm. In this study, the presence of borides was identified using XRD analysis; see Figures 2a and 2b. XRD patterns show that the boride layer consists of borides such as SB and S_2B (S=Metal; Fe, Cr). X-ray diffraction analysis of boride layers on the surface of specimens revealed peaks of FeB, Fe_2B, CrB, Cr_2B and MoB (Figs.2a and 2b).

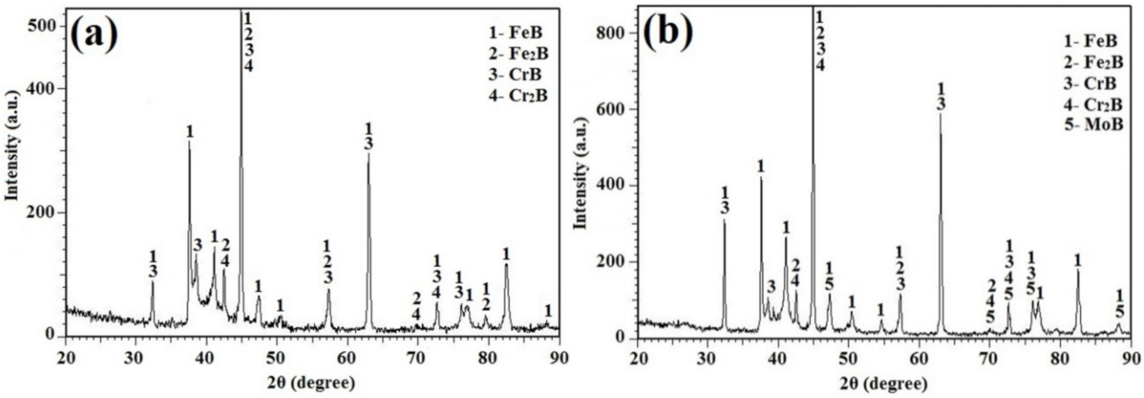

Figure 2: X-ray diffraction patterns of borided cold work tool steel: a) 850 ºC - 6h, b) 950 ºC - 6h

The hardness of the borides formed on the surface of the cold tool steel ranged from 1806 to 2342 $HV_{0,05}$, whereas Vickers hardness values of the untreated the steels was 428 $HV_{0,05}$, as shown in Figure 3.

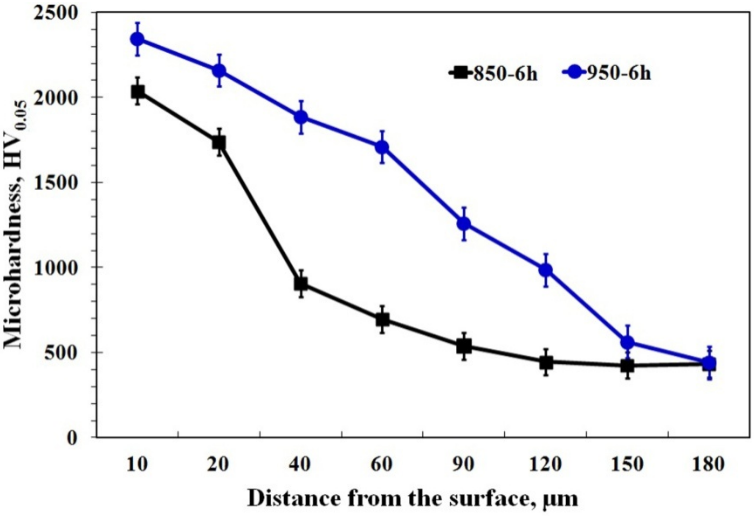

Figure 3: The variation of hardness depth in the borided steel.

Figures 4a and 4b show the SEM and EDS analyses carried out on the unborided cold work tool steel after the corrosion test.

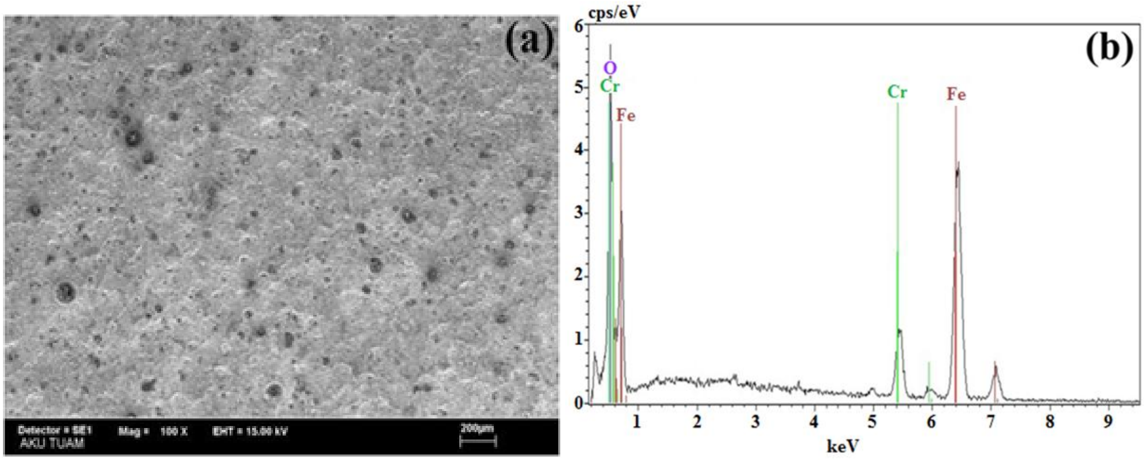

Figure 4: SEM and EDS analyses after corrosion of the unborided steel surface in 4% M HCl solution: a) SEM, b) EDS.

Figures 5a-5d show the SEM and EDS analyses carried out on the steel borided at a temperature of 850 and 950 ºC for 6 h, after the corrosion tests. Pitting corrosion has been occurred (Figure 4 and 5). Oxides were observed on the surface of the specimen after the corrosion test. Oxide peak intensities formed deeper down in the surface of the borided specimens compared to the unborided specimen (Fig. 4b, 5b, 5d). The corrosion resistance of boron-coated steel usually depends on the characteristic features of coatings such as the number of microcracks and porosities. These porosities negatively affect the firmness of coatings and significantly reduce the corrosion resistance.

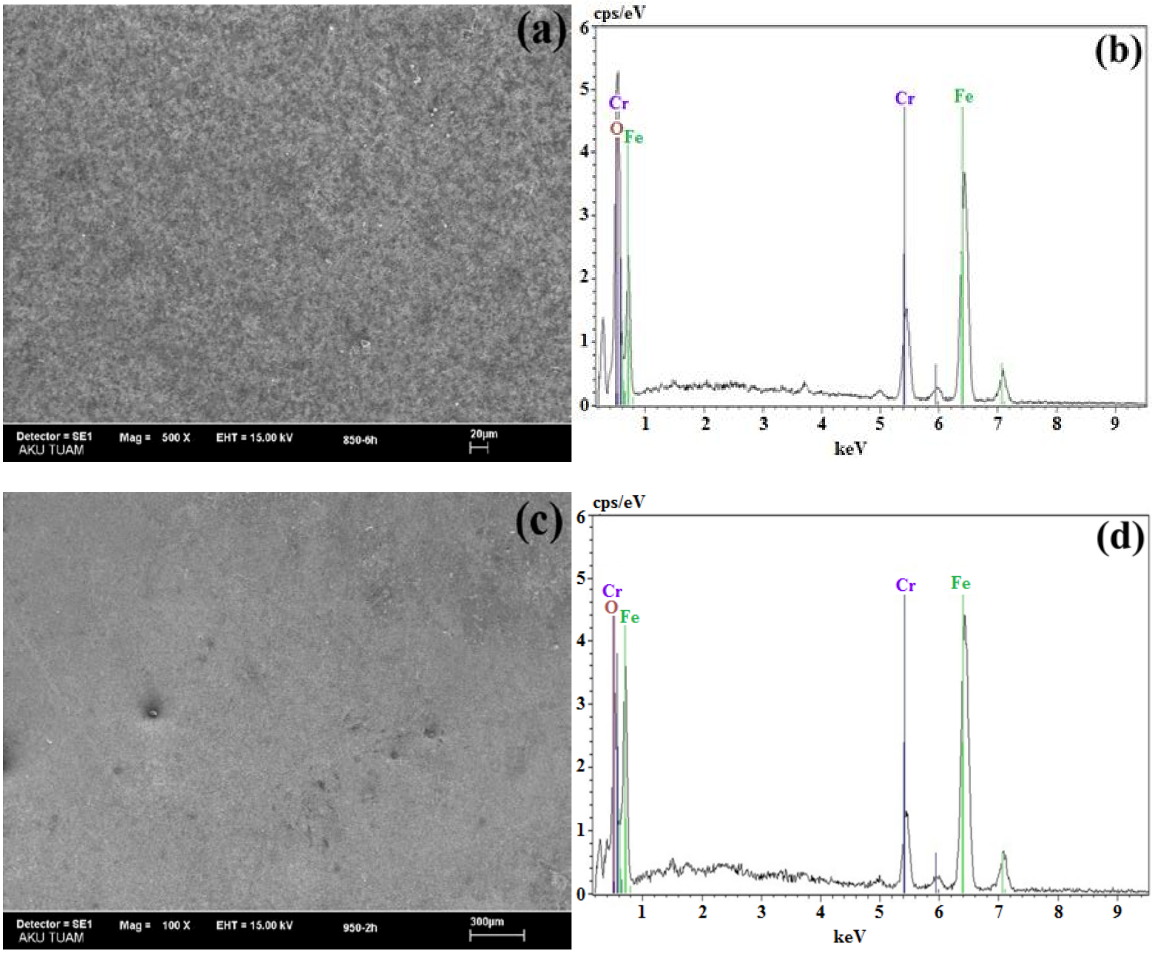

Figure 5: SEM and EDS analyses of borided the steel surface in 4% M HCl solution: a) 850 ºC - 6h SEM, b) 850 ºC - 6h EDS, c) 950 ºC - 6h SEM, d) 950 ºC - 6h EDS.

At the end of these tests, the variation of weight loss depending on time was obtained. The variation for the 4% M HCl solution is presented in Fig. 6.

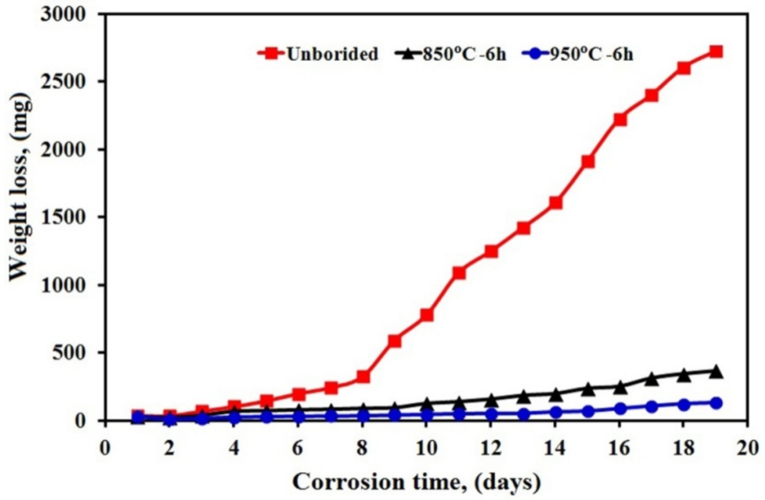

Figure 6: Weight loss of immersion tests of the borided cold work tool steel in 4% M HCl solution.

Weight loss in the unborided specimen after the corrosion was observed to increase rapidly with the increase in processing time. It was detected that while the weight loss in the corrosion test solution during day 8 was 592.18 mg the corrosion weight loss of the raw specimen increased to 2675.93 mg after day 19 for unborided cold work tool steel (Fig.6). It was detected that while the weight loss in the corrosion test solution during day 8 was 161.47 mg the corrosion weight loss of the raw specimen increased to 347.12 mg after day 19 for borided cold work tool at a temperature of 850 ºC for 6h (Fig.6). It was detected that while the weight loss in the corrosion test solution during day 8 was 79.85 mg the corrosion weight loss of the raw specimen increased to 150.36 mg after day 19 for borided cold work tool at a temperature of 950 ºC for 6h (Fig.6). While the weight loss of the unborided specimen was 2675.93 mg this value dropped to 150.36 mg as a result of the boriding process for the cold work tool. The solubility of corrosion in the unborided specimen increased 17-fold.

As shown in the graphic curves in corrosive environment, the solubility of corrosion decreased with the boriding treatment of the specimens. In addition, it was observed that the decreased solubility of corrosion in the borided specimens led to a decrease in the amount of material loss. The solubility of corrosion in the borided specimens was observed to be 8-17 (850 ºC - 6h and 950 ºC - 6h) times lower than in the unborided specimens. The corrosion resistances of the cold work tool steel increased with the boriding process.

4. DISCUSSION

Figure 1a and 1b shows optical microstructures of solid borided tool steel. The thickness of the boride layer increased with the increase in boriding time. The characteristics of this boride layer depend on the physical state of the boride source used, boriding temperature, treatment time, and properties of the borided material [18-20]. XRD results showed that boride layers formed on the tool steel contained the FeB, Fe_2B, CrB, Cr_2B and MoB phases in Figure 2. The boride layers mainly consist of intermetallic phases (FeB, Fe_2B and CrB) as a result of diffusion of boron atoms from the boriding compound to the metallic lattice with respect to the holding time. The properties of these boride layers are known to a large extent by the help of these phases [21-24]. Micro-hardness measurements were done from the surface to the interior along a line to see variation of hardness of the boride layer, transition zone and matrix, respectively in Figure 3. When the hardness of the boride layer is compared with the matrix, boride layer hardness is approximately five times greater than that of matrix. High hardness values were obtained in tool steel due to the FeB, CrB and MoB phases. Ozbek et al. [25] borided AISI 316L steel by ekabor powders and found that higher boriding temperatures resulted in higher hardnesses due to the formation of the harder FeB and CrB phase. Sen et al. [26, 27] borided cold work tool steels by pack and salt bath boriding and found that prolonged boriding time and high temperatures decreased fracture toughness values due to the formation of FeB phases and increased boride layer hardness. After the corrosion test, porosity and pits were observed to form on the borided specimen. The corrosion resistance of boron-coated steel usually depends on the characteristic features of coatings such as the number of microcracks and porosities. These porosities negatively affect the firmness of coatings and significantly reduce the corrosion resistance. The number of voids such as these is associated with the microstructure of the coating [28-31]. As result of the boriding process the corrosion resistances of the cold work tool steel increased.

5. CONCLUSIONS

The following conclusions may be derived from the present study.

- Boride types formed on the surface of the cold work tool steel have a smooth morphology.
- The boride layer thickness on the surface of the cold work tool steel was obtained, depending on the chemical composition of substrates, 13.14-120.82 μm.
- The polyphase boride coatings that were thermo chemically grown on the cold work tool steel were constituted by the FeB, Fe_2B, CrB, Cr_2B and MoB phases.
- The surface hardness of the borided steel was in the range of 1806-2342 $HV_{0,05}$, while for the untreated the steel substrate it was 428 $HV_{0,05}$.
- The corrosion resistance of borided cold work tool steel 8–17- fold.
- Pitting corrosion has been occurred on the samples.
- The corrosion resistance of the cold work tool steel was improved by the boriding process.

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