A. Calik, N. Ucar*, M.S. Karakas and H. Tanis

Pack-Boriding of Pure Iron with Powder Mixtures Containing ZrB_2

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Abstract: Boriding of pure iron was investigated using the powder pack method with boriding powder mixtures containing different weight fractions of ZrB_2 (5 %, 10 %, 15 % and 20 %). The samples were borided in an electric resistance furnace for an exposure time of 4 h at 1,173 K temperature under atmospheric pressure. Borided samples were characterized by optical microscopy, X-ray diffraction analyses and microhardness tests. Results showed that the boride layers consisted mainly of FeB and Fe_2B phases. No significant difference in boride layer thicknesses (average 140 μm) could be observed as a function of ZrB_2 content. The needle-like morphology of the boride layer became more prominent with increasing weight fraction of ZrB_2 in the boriding powders. The average microhardness of the boride layer decreased with increasing ZrB_2 content due to changes in the morphology of the boride layer.

Keywords: boriding, boride layer, boriding agent, microhardness, ZrB_2

Introduction

Iron is the second most abundant metal in Earth's crust, after aluminium. When reduced from its ore, pure iron is soft and susceptible to corrosion. The use of surface coatings opens up the possibility for material design in iron and steel for which certain properties such as surface hardness and corrosion resistance can be improved. One such surface coating technique is boriding, a thermochemical surface treatment in which boron atoms diffuse into the surface of the workpiece to form hard borides with the base material. Boriding can be performed in a

solid, liquid or gaseous medium and is applicable to iron-based alloys as well as to alloys of nickel, cobalt and titanium [1–10]. While showing some promise, liquid- and gas-phase boriding techniques have not become popular due to toxicity issues.

In the literature [11–13], it has been shown that borided materials exhibit significantly higher surface hardness compared to their untreated counterparts and improved abrasive and adhesive wear resistance, due to the hard boride phases grown on the surface and also due to diffusion of boron into the substrate. The composition and thickness of the boride layer formed on the surface can be significantly altered by changing certain parameters which include, but are not limited to, the boriding source, time, temperature and the chemical composition of the substrate. Corresponding to this, it has been shown that longer boriding times and higher treatment temperatures usually result in the greater coating layer thickness [14–16]. Various investigations have also shown that boriding agents and their compositions in the boriding medium can have important effects on the formation of boride layers and phases [17–19]. Calik [19] reported that the average microhardness of the boride layers can range between 1,450 and 1,651 HV, depending on the size of the powders in the boriding source. The thickness of the boride layer increases with decreasing particle size of the boriding powders and increasing boriding temperature.

Zirconium diboride (ZrB_2) has attracted considerable attention due to its excellent combination of properties such as high melting point, high hardness, high thermal and electrical conductivity, high-temperature strength and thermal shock resistance. Bliznakov et al. [20] showed that the treatment of steel surfaces with ZrB_2 leads to complex boridation-zirconization, resulting in enhanced hardness values in comparison to that of iron borides. Zakhariyev et al. [21] reported that coatings up to 1 mm in thickness can be produced by boriding treatments involving ZrB_2 as the main additive. The coatings were found to consist of ZrO_2 , ZrB_2 and Fe_2B phases. The main goal of the current study is to investigate the microstructure and morphology of boride layers grown on the surface of pure iron by pack boriding using powders containing ZrB_2 in different concentrations as the boron source.

***Corresponding author: N. Ucar**, Department of Physics, Süleyman Demirel University, Isparta 32260, Turkey,
E-mail: nazmucar@yahoo.com

A. Calik, Department of Manufacturing Engineering, Applied Sciences University of Isparta, Isparta 32260, Turkey

M.S. Karakas, Department of Metallurgical and Materials Engineering, Konya Technical University, Konya 42130, Turkey

H. Tanis, Department of Manufacturing Engineering, Süleyman Demirel University, Isparta 32260, Turkey

Experimental method

Pure iron samples (99.97% purity, obtained from Alfa Aesar) were packed in boriding sources composed of 5 wt.% B_4C and 5 wt.% KBF_4 with varying concentrations of ZrB_2 and SiC as shown in Table 1. Ekrit[®] powder (finely ground SiC , supplied from Bortech GmbH, Germany) was also added on top of the pack as a cover layer to prevent oxidation. The boriding process was carried out at a temperature of 1,173 K for 4 h.

Table 1: Compositions of the different boriding sources (wt.%).

Boriding source	ZrB_2	SiC	B_4C	KBF_4
ZB0	0	90	5	5
ZB1	5	85	5	5
ZB2	10	80	5	5
ZB3	15	75	5	5
ZB4	20	70	5	5

Microstructural analysis of borides formed on cross-sections of the borided pure iron samples was carried out using optical and scanning electron microscopy. The presence of borides and other phases formed on the surface of the borided samples was determined by using an X-ray

diffractometer (Rigaku D-MAX 2200) with $CuK\alpha$ radiation of 0.15418 nm wavelength. The thickness of the boride layer was measured from optical micrographs. For the measurement of boride layer thickness, only the needles which penetrate most deeply into the substrate were selected as suggested in Ref [22, 23].

To determine the hardness profiles of the borided samples, microhardness measurements were made on cross-sections perpendicular to the borided surface by means of a Vickers indenter with a load of 100 g and dwell time of 15 s. Before microhardness testing, a standard specimen was used for calibration. To ensure the reliability of the results, a minimum of five measurements were made at each depth to obtain average microhardness values.

Results and discussion

The cross-sections of optical micrographs of pure iron borided with the ZB1, ZB2, ZB3 and ZB4 powders at 1,173 K for 4 h are shown in Figure 1. As seen in the figure, the boride layers exhibit the characteristic needle-like morphology. Two distinct regions are identified in the cross-sections of the borided pure iron surfaces: the double-phase boride layer and the substrate unaffected

Figure 1: Cross-sectional optical microscopy images of pure Fe borided at 1,173 K for 4 h using (a) ZB1, (b) ZB2, (c) ZB3 and (d) ZB4 powders.

by boron diffusion. Crack formation is present within the double-phase boride layer, which is common in borided iron and steel [24–26]. The micrographs also show that increasing the ZrB_2 content in the boriding source does not result in significant difference in the thickness of the boride layers.

The average boride layer thickness value of borided pure iron sample borided with powders containing ZrB_2 additions varies between 138 and 141 μm , while it is 139 μm for the pure iron sample borided with powders without ZrB_2 addition. However, when the micrographs in Figure 1 are compared, it can be seen that addition of ZrB_2 tends to cause greater variation between the peaks and valleys in the double-phase boride layer. Addition of ZrB_2 to the boriding powder, therefore, has a negative effect on the boriding process, hindering the diffusion of boron into the substrate.

According to X-ray diffraction (XRD) analyses, the boride layers in the borided pure iron samples are composed of FeB , Fe_2B and also ZrB_2 (Figure 2). The reason

why ZrB_2 does not appear in the optical micrographs in Figure 1 but appears in the XRD patterns in Figure 2 should be considered as due to the holding or adhesion of ZrB_2 on the surface due to high boriding temperature.

Microhardness measurements were carried out from the surface to the interior on cross-sections of the borided specimens. As seen in Figure 3, the hardness of the boride layer is approximately ten times that of the matrix. This is a consequence of the presence of hard boride phases as determined by optical microscopy and XRD analyses. On the other hand, it can be seen again from the figure that ZrB_2 addition in the boriding source decreases the average hardness of the resulting boride layer. Summarizing, the results of the current study show that the presence of ZrB_2 in the boriding source does not result in the formation of a surface coating with enhanced hardness compared to the hardness of iron borides, and does not have a positive influence on boride layer thickness, contrary to the results published by Bliznakov et al. [20] and Zakhariyev et al. [21].

Figure 2: X-ray diffraction patterns obtained from the surface of pure Fe borided at 1,173 K for 4 h using (a) ZB1, (b) ZB2, (c) ZB3 and (d) ZB4 powders.

Figure 3: Change in microhardness values from boride surface to substrate for borided pure Fe.

Conclusions

In this study, the effect of boriding powders with varying ZrB_2 contents on the boriding behaviour of pure iron was investigated. The following conclusions can be drawn:

- Two distinct regions were identified in the cross-sectional optical micrographs of the borided samples: The boride layer and the substrate unaffected by boron diffusion.
- The boride layer exhibited needle-like morphology and consisted mainly of FeB and Fe_2B . ZrB_2 was additionally detected through XRD analysis.
- No significant difference in boride layer thickness as a function of ZrB_2 content was observed.
- The microhardness in the boride layer decreased with increasing ZrB_2 content due to the hindering of boron diffusion into the surface.

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References

- [1] D. Mu, B.-L. Shen, C. Yang and X. Zhao, *Vacuum*, 83 (2009) 1481–1484.
- [2] I. Özbek, H. Akbulut, S. Zeytin, C. Bindal and A.H. Ucisik, *Surf. Coat. Technol.*, 126 (2000) 166–170.
- [3] N. Ueda, T. Mizukoshi, K. Demizu, T. Sone and M. Kawamoto, *Surf. Coat. Technol.*, 126 (2000) 25–30.
- [4] A. Calik, M.S. Karakas, N. Ucar and F. Unuvar, *Kovove Mater*, 52 (2014) 107–112.
- [5] D. Mu, C. Yang, B.-L. Shen and H. Jiang, *J. Alloys Compd.*, 479 (2009) 629–633.
- [6] Z.T. Zahariev and M.I. Marinov, *J. Alloys Compd.*, 201 (1993) 1–3.
- [7] O. Knotek, E. Lugscheider and K. Leuschen, *Thin Solid Films*, 45 (1977) 331–339.
- [8] N. Makuch, M. Kulka, M. Keddad, S. Taktak, V. Ataibis and P. Dziarski, *Thin Solid Films*, 626 (2017) 25–37.
- [9] B. Sarma, N.M. Tikekar and K.S. Ravi Chandran, *Ceram. Int.*, 38 (2012) 6795–6805.
- [10] P. Kaestner, J. Olfe and K.-T. Rie, *Surf. Coat. Technol.*, 142–144 (2001) 248–252.
- [11] E.A. De Almeida, C. Da Costa, J. Milan, A.P. Krelling and A. Galiotto, *Matéria*, 22 (2017) 1517–1526.
- [12] I. Gunes and M. Ozcatal, *Mater. Tehnol.*, 50 (2016) 269–274.
- [13] E. Cardenas, R. Lewis, A.M. Perez, J.L. Ponce, F.P. Pinal, M.O. Dominguez and E.D. Arreola, *Adv. Mech. Eng.*, 8 (2016) 1–10.
- [14] Y. Kayali, I. Gunes and S. Ulu, *Vacuum*, 86 (2012) 1428–1434.
- [15] N. Ucar, O.B. Aytar and A. Calik, *Mater. Tehnol.*, 46 (2012) 621–625.

- [16] A. Milinovic, D. Krumes and R. Markovic, *Teh. Vjesn.*, 19 (2012) 27–31.
- [17] M. Kul, K.O. Oskay, A. Temizkan, B. Karaca, L.C. Kumruoglu and B. Topcu, *Vacuum*, 126 (2016) 80–83.
- [18] B. Bouarour, M. Keddou, O. Allaoui and O. Azouani, *Metall. Res. Technol.*, 111 (2014) 67–73.
- [19] A. Calik, Effect of powder particle size on the mechanical properties of boronized EN H320 LA steel sheets, *ISIJ Int*, 53 (2013) 160–164.
- [20] G. Bliznakov, Z. Zakhariev, I. Tzolovsky and S. Velichkov, *J. Less Common Met.*, 82 (1981) 119–123.
- [21] Z. Zakhariev, M. Marinov, T. Penyashki and P. Tsokov, *J. Alloys Compd.*, 459 (2008) 501–503.
- [22] C.M. Brakman, A.W.J. Gommers and E.J. Mittemeijer, *J. Mater. Res.*, 4 (1989) 1354–1370.
- [23] A.G. Von Matuschka, *Boronizing*, Heyden and Son Inc., Philadelphia (1980).
- [24] O. Ozdemir, M. Usta, C. Bindal and A.H. Ucisik, *Vacuum*, 80 (2006) 1391–1395.
- [25] K.-H. Habig and R. Chatterjee-Fischer, *Trib. Int.*, 14 (1981) 209–215.
- [26] I. Altinsoy, T. Yener and A. Kizilaslan, 18th International Metallurgy and Materials Congress Proceedings, IMMC, September 29 – October 1, Istanbul, UCTEA Chamber of Metallurgical and Materials Engineers, Istanbul (2016), pp. 1–4.