Boriding of Binary Ni–Ti and Ternary Ni–Ti–Cu Shape Memory Alloys

N. Ucar[a,*], N. Turku[a], A.F. Ozdemir[a] and A. Calik[b]

[a]Physics Department, Faculty of Arts and Sciences, Suleyman Demirel University, Isparta, Turkey

[b]Manufacturing Engineering Department, Faculty of Technology, Suleyman Demirel University, Isparta, Turkey

In this work, the boriding of binary (Ni–Ti) and ternary (Ni–Ti–Cu) shape memory alloys was carried out in a solid medium at 1173 K for 8 h using the powder pack method with Ekabor-Ni powders. Characterization of boride layer formed on the surface of alloys was identified by optical microscopy and scanning electron microscopy. TiB_2, NiB_2 and SiC phases in the boride layer of borided binary (Ni–Ti) and ternary (Ni–Ti–Cu) shape memory alloys was confirmed by X-ray diffraction analysis. The microhardness and thickness of the boride layers were measured. The obtained hardness values show a hardness anomaly due to porosity and structural defects with increase of Cu content, while a decrease in the value of hardness moving from the boride layer to main structure was observed.

1. Introduction

Various surface treatment methods aimed at improving wear resistance, corrosion and mechanical properties are described in many recent works [1–4]. One of the methods used to improve characteristics is boriding [5–7]. In this method [2, 3, 7–10], boron atoms, because of their relatively small radii can easily diffuse into the substrate material to form hard boride layers. In the literature [11–14], it has been shown that the boride layer thickness is influenced by alloying elements which can modify the active boron flux by entering the iron boride lattice. Corresponding to this, it has been shown that the alloy elements such as C, Cr, and Mo appear to be lower in the vicinity of the boride layer because of less solubility. The deficiency of C, Cr, and Mo results in a negative effect on the boride layer in terms of both thickness and morphology [10, 15, 16]. On the other hand, C, which is insoluble in iron borides, concentrates strongly at the (boride layer/substrate) interface [17, 18].

Ti–Ni alloys exhibit good properties in strength, ductility, resistance to corrosion and biocompatibility, which are important for practical use, in addition to excellent shape memory effect characteristics [4, 19, 20]. NiTiCu alloys obtained by replacing a part of Ni and Ti atoms by Cu in the equiatomic NiTi alloy have attracted wide interest because of a variety of advantages in practical use [4, 20, 21]. It has been shown that the addition of Cu to Ni–Ti does not increase the transformation temperatures, but it can rise the stability of the alloy during temperature changes and mechanical loading [20]. In addition, Cu addition, as a ternary alloying element, results in increased characteristic temperatures of the martensitic transformation, when compared to a binary NiTi

alloys [20]. Moreover, Cu causes good stability of characteristic temperatures and good corrosion resistance, narrow transformation hysteresis and prevention of Ti_3Ni_4 precipitation [22, 23].

Recently, intensive effort has been put into adopting the nonconventional production techniques such as powder metallurgy, melt-spinning or twin roll casting for the manufacture NiTi-based alloys [24]. In addition, a number of studies have previously been carried out involving nanoindentation and microstructural characterization of shape memory alloys, in both bulk [25, 26] and thin film forms [27–29]. However, no investigation has yet been reported on boriding of binary (Ni–Ti) and ternary (Ni–Ti–Cu) shape memory alloys. In this study, the morphology, boride layer thickness and hardness behaviour of borided binary (Ni–Ti) and ternary (Ni–Ti–Cu) shape memory alloys were studied.

2. Experimental method

Chemical composition of alloys for experiments is presented in Table I.

TABLE I

Chemical composition of used binary (Ni–Ti) and ternary (Ni–Ti–Cu) shape memory alloys [wt.%].

Material	Ni	Ti	Cu
A	59.36	40.64	–
B	64.39	26.40	9.20
C	53.07	30.36	16.56

The samples were cut to dimensions of $2 \times 2 \times 15$ mm^3. Boriding of these samples was achieved in a solid medium using the powder pack method with Ekabor-Ni powders containing SiC as a diluent. The pack was heat treated in an electrical resistance furnace for exposure time 8 h at 1173 K under atmospheric pressure. The thickness

———

*corresponding author; e-mail: nazimucar@sdu.edu.tr

of borides was measured by means of a digital thickness measuring instrument attached to an optical microscope (Nikon MA100). The boride layer thickness values given in the results section are averages of at least 12 measurements. The presence of borides on the surface of the boronized alloys was determined by using the X-ray diffractometer (Rigaku D-MAX 2200) with a Cu K_α radiation of 0.15418 nm wavelength. Metallographic sections were prepared to observe morphological details by the use of optical and scanning electron microscopy (SEM, JEOL5600LV). To determine the hardness of the alloys, a Vickers microhardness tester with a load of 100 g and dwell time 15 s was used. Many indentations were made on each coating film under each experimental condition to check the reproducibility of hardness data.

3. Results and discussion

The cross-sections of optical micrographs of the boronizing of A, B and C shape memory alloys at 1173 K for 8 h are shown in Fig. 1. As seen from the figure, borides formed on the surface displayed a more diffuse morphology compared to the sawtooth morphology commonly observed in A, B and C shape memory alloys. Three distinct regions were identified on the surface of A, B and C shape memory alloys: (i) borides, (ii) transition zone and (iii) matrix.
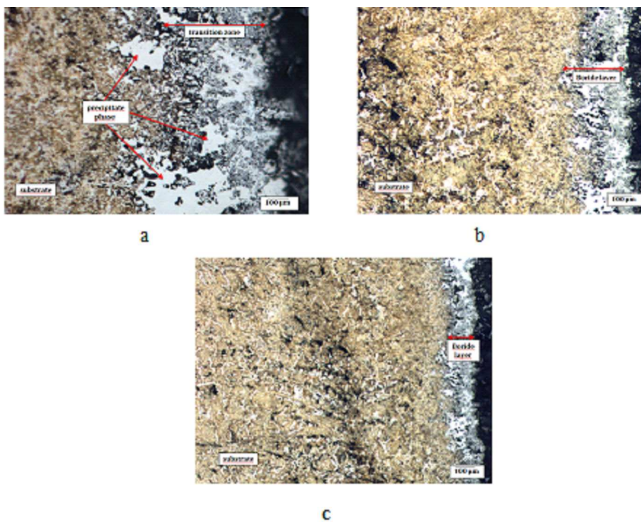

Fig. 1. SEM images of the cross-sections of shape memory alloys A, B, C borided for 8 h at 1173 K.

Figure 1a shows that the boride layer in the A binary shape memory alloy is wider compared to the ternary alloys and additionally contains precipitate phases. The morphology of the boride layers became smoother with increase of Cu content in the B and C ternary shape memory alloys (Fig. 1b and c). Excessive grain growth in the transition region was observed in all borided specimens. Both thickness and length of teeth relative in the boride layer and the boride layer thickness decrease

with increasing Cu content. Compared to the A shape memory alloy, boron diffusion in B and C shape memory alloys was more difficult because of significant migration of Cu atoms into the matrix. As a result, the thickness of boride layer formed surface of the ternary Ni–Ti–Cu alloys is lower. The obtained thickness values were 138, 90, and 36 μm for A, B, and C shape memory alloys, respectively (Table II). Conversely, it has been shown that the Cu does not significantly affect the boride layer thickness while Si as an alloying element in the substrate considerably decreases boride layer thickness in borided Fe–8Si [30] and Fe–8Cu [31] binary alloys.

TABLE II

Boride layer thickness and microhardness values of borided binary (Ni–Ti) and ternary (Ni–Ti–Cu) shape memory alloys.

Material	Layer thickness [μm]	Microhardness [$HV_{0.1}$]
A	138	1819
B	90	2733
C	36	2282

On the other hand, the porosity was seen in the boride layer of the samples. However, increase of Cu content resulted in the increase of porosity in the boride layer and transition layer. In addition to the porosity, light-colored precipitates (regions) were detected in the transition layer, especially in the binary A shape memory alloy. The amount and size of light-colored regions generally decreases with the amount of Cu (Fig. 1a–c). The light-colored regions belong to isolated copper precipitates, indicating that Cu does not dissolve in the boride layer and it does not form a Cu_xB_y phase (Fig. 2). The same precipitates have been also obtained on borided Fe–8Cu alloys [31], where it was shown that light gray region, has high amounts of Cu and relatively less amounts of Fe.
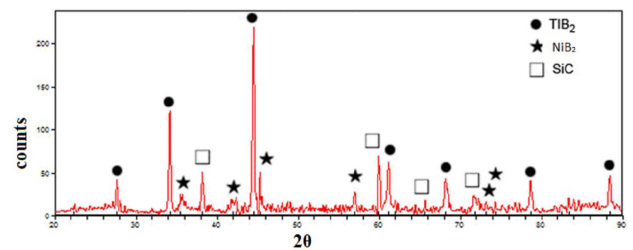

Fig. 2. XRD pattern of B shape memory alloy borided for 8 h at 1173 K.

Figure 3 shows the microhardness profile measured on the cross-section of B shape memory alloy borided at 1173 K for 8 h under atmospheric pressure.

In this figure, it is possible to observe how the hardness of borided samples changes from the boride layer to matrix. It is also seen from Fig. 3 that the hardness of boride layer is much higher than that of the matrix. The high hardness of the surface is mainly a result of the presence of hard phases in the boride layer, but is additionally due
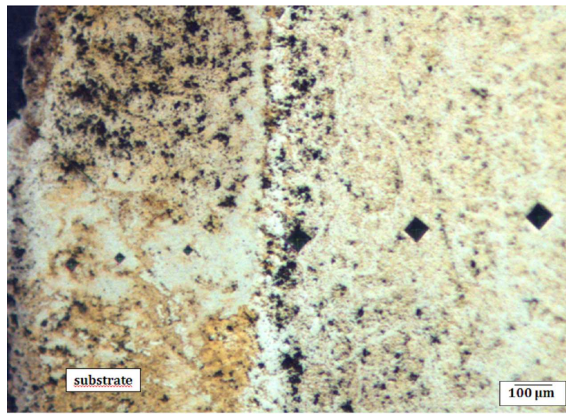
Fig. 3. View of Vickers indentations from the outer layer to interior of the B shape memory alloy borided shape memory alloy B, 1173 K for 8 h.

to solid solution hardening between Cu and boron atoms in the matrix. Summarizing, after the boriding treatment at 1173 K for 8 h, the surface hardness was increased by a factor close to 6 in comparison with the matrix. In contrast, although hardness decreased with distance from the surface in all three alloys, some anomalies were observed in the measured hardness values. The obtained hardness values were 1819, 2733 and 2282 $HV_{0.1}$ for A, B, and C shape memory alloys, respectively (Table II). We think that the fluctuated hardness in the borided A, B, and C shape memory alloys, hardness anomaly, may be due to structural defects such as porosity and cracks with boriding process. Although the study on the microstructure and hardness of borided binary (Ni–Ti) and ternary (Ni–Ti–Cu) shape memory alloys is not to be seen in literature, the obtained results are not compared with results from the literature.

4. Conclusions

The results of the current study can be summarized as follows:

- The microstructure of boride binary (Ni–Ti) and ternary (Ni–Ti–Cu) shape memory alloys showed three distinct regions: the boride layer, the transition zone, and the matrix. The prominent phases formed in the surface layer of the boronized alloys were TiB_2 and NiB_2 which were revealed by X-ray diffraction analyses.

- The alloys showed somewhat inconsistent results in terms of boriding behavior. The morphology and overall appearance of the boride layer displayed varying results with increasing Cu concentration. It can be said that Cu addition to binary Ni–Ti shape memory alloys, in substitution for Ni and Ti, can significantly alter the microstructure morphology of alloy.

- It was observed that the boride layer thickness decreased with increase of Cu content due to effects of alloying elements.

- Some anomalies in the hardness of the boride layers were observed, which were attributed to porosity and structural defects.

References

[1] C. Meric, S. Sahin, B. Backir, N.S. Koksal, *Mater. Des.* **27**, 751 (2006).

[2] M.A. Bejar, E. Moreno, *J. Mater. Proc. Technol.* **173**, 352 (2006).

[3] Y.L. Huang, I.N.A. Oguocha, S. Yannacopoulos, *Wear* **258**, 1357 (2005).

[4] T. Goryczka, J.V. Humbeeck, *J. Achiev. Mater. Manufact. Eng.* **17**, 65 (2006).

[5] S. Sahin, C. Meric, *Mater. Res. Bull.* **37**, 971 (2002).

[6] I. Campos, O. Bautista, G. Ramírez, M. Islas, J. De La Parra, L. Zúñiga, *Appl. Surf. Sci.* **243**, 431 (2005).

[7] X. Qiao, H.-R. Stock, A. Kueper, C. Jarms, *Surf. Coat. Technol.* **131**, 291 (2000).

[8] C. Bindal, A.H. Ucisik, *Vacuum* **82**, 90 (2008).

[9] H. Celikkan, M.K. Ozturk, H. Aydin, M.L. Aksu, *Thin Solid Films* **515**, 5348 (2007).

[10] A.K. Sinha, *Boronizing*, ASM Handbook, J, OH, USA 1991.

[11] S. Sen, U. Sen, C. Bindal, *Vacuum* **77**, 195 (2005).

[12] I. Ozbek, C. Bindal, *Surf. Coat. Technol.* **154**, 14 (2002).

[13] H. Kemi, C. Sasaki, M. Kitamura, N. Satomi, Y. Ueda, M. Nishikawa, *J. Nucl. Mater.* **266**, 1108 (1999).

[14] L.L. Oian, G.A. Stone, *J. Mater. Eng. Perform.* **4**, 59 (1995).

[15] I. Campos, G. Ramirez, U. Figueroa, J. Martinez, O. Morales, *Appl. Surf. Sci.* **253**, 3469 (2007).

[16] I. Gunes, *Sadhana* **38**, 527 (2013).

[17] S. Taktak, S. Tasgetiren, *J. Mater. Eng. Perform.* **15**, 570 (2006).

[18] I. Uslu, H. Comert, M. Ipek, O. Ozdemir, C. Bindal, *Mater. Des.* **28**, 55 (2007).

[19] M.T. Ochoa-Lara, H. Flores-Zúñiga, I. Estrada-Guel, R. Martínez-Sánchez, *Microsc. Microanal.* **11**, 1854 (2005).

[20] A.J. Muir Wood, S. Sanjabi, Y.Q. Fu, Z.H. Barber, T.W. Clyne, *Surf. Coat. Technol.* **202**, 3115 (2008).

[21] A.A. Atiyah, A. Ali, N.M. Dawood, *Arab. J. Sci. Eng.* **40**, 901 (2015).

[22] T.H. Nam, T. Saburi, Y. Nakata, K. Shimizu, *Mater. Trans. JIM* **31**, 1050 (1990).

[23] T. Fukuda, T. Kakeshita, M. Kitayama, K. Saburi, *J. Phys. IV (France)* **05**, 717 (1995).

[24] T. Goryczka, P. Ochin, *J. Mater. Proc. Technol.* **162**, 178 (2005).

[25] W. Ni, Y.-T. Cheng, D.S. Grummon, *Appl. Phys. Lett.* **80**, 3310 (2002).

[26] K. Gall, K. Juntunen, H.J. Maier, H. Sehitoglu, Y.I. Chumlyakov, *Acta Mater.* **49**, 3205 (2001).

[27] H.D. Espinosa, B.C. Prorok, M.J. Fischer, *J. Mech. Phys. Solids* **51**, 47 (2003).

[28] W. Ni, Y.-T. Cheng, M. Lukitsch, A.M. Weiner, L.C. Lev, D.S. Grummon, *Wear* **259**, 842 (2005).

[29] X.-G. Ma, K. Komvopoulos, *Appl. Phys. Lett.* **83**, 3773 (2003).

[30] M. Tarakci, Y. Gencer, Y. Azakli, U. Sahinturk, *J. Fac. Eng. Archit. Gazi Univ.* **28**, 645 (2013).

[31] S. Cengiz, Y. Gencer, M. Tarakci, Y. Azakli, *J. Fac. Eng. Archit. Gazi Univ.* **30**, 339 (2015).