

Special Issue of the 6th International Congress & Exhibition (APMAS2016), Maslak, Istanbul, Turkey, June 1–3, 2016

Effect of H_3BO_3 on the Corrosion Properties of Ni–B Based Electroplating Coatings

A. KARABULUT^{a,*}, M. DURMAZ^a, B. KILINC^b, U. SEN^a AND S. SEN^a

^aSakarya University, Metallurgical and Materials Engineering, Engineering Faculty, 54187 Sakarya, Turkey

^bSakarya University, Metallurgical and Materials Engineering, Institute of Arts and Sciences, 54187 Sakarya, Turkey

In this study the effect of H_3BO_3 on the properties of Ni–B coating formed on the AISI 1020 steel surface produced with electroplating process was investigated. Synthesis of the coatings was done using acidic electroplating bath. Coating process was carried out within a standard cell with three electrode system using platinum as auxiliary and Ag/AgCl electrode as a reference electrode onto AISI 1020 steel substrate. Then, heat treatment was applied to coatings at 400 °C during a period of 1 h. The coated samples were analyzed by optical microscope, scanning electron microscope, and X-ray diffraction. Micro hardness measurements of the coatings were realized. The study reveals that the Ni–B anti corrosion coating is amorphous in their as-plated condition and upon heat treatment at 400 °C for 1 h, Ni–B coatings crystallize and produce nickel borides and nickel in the coatings. The results indicated the presence of Ni_2B , Ni_3B and Ni phases.

DOI: [10.12693/APhysPolA.131.147](https://doi.org/10.12693/APhysPolA.131.147)

PACS/topics: 81.15.Pq

1. Introduction

Ni–B and Ni–P graded coatings have been proposed as possible replacement coatings for the existing hard chromium coatings [1–3]. Ni–B alloys have been widely used as a protective coating and have a great potential to replace the hard chromium coating owing to their good mechanical and wear-resistant properties, as well as the well-controlled internal stress [4–7]. Electrolytic coatings are also commonly used in the industry because they have a shiny finish well adhering to different materials with complicated geometries and can be made at reasonable cost in an environment friendly solution [5].

The Ni–B deposits were determined to have wettability properties that are comparable to those of Ni–P and Ni–B–P deposits but inferior to those of Ni–W–P deposits [8]. Generally, a hard film is formed on the surface of sliding parts to improve wear and abrasion resistance. Usually the film is electroplated Cr (chromium). An alternative technology has been developed due to environmental problems. Electroless Ni plating was adopted because of its quality, cost, and ease of mass production. Moreover, it is known that hardness is increased with post annealing. In this work, we report briefly on some of the properties of electroplating Ni–B amorphous deposits [9].

2. Experimental method

2.1. Substrate materials

Substrate material used in this study was AISI 1020 steel. The chemical composition of the test material is given in Table I. AISI 1020 steel samples were semicylinder shaped with the 10 mm in diameter and 25 mm

in height. All the samples were ground using 1200-grid emery paper to get surface finish before electroplating.

TABLE I

The chemical composition of substrate materials [wt%].

Steel	C	Mn	S	P	Fe
AISI 1020	0.2	0.35	0.03	0.02	balance

2.2. Characterization and analysis

H_3BO_3 powder was milled for 2 h by using a planetary mill. The particle size distribution of H_3BO_3 powders were measured using a laser particle size analyzer COULTER-LS130 before and after the milling process. The hardness measurement was carried out by the Vickers hardness test. The microstructure of coatings was analyzed using a scanning electron microscope (SEM) (Vega 2 TESCAN, Czech Republic) and optical microscope (OM). The phase analysis was performed via X-ray diffraction (XRD; step: 0.02°, step time: 1.0 s). Corrosion tests of Ni–B based coatings were performed in a three-electrode system test unit with a graphite counter electrode and a calomel reference electrode using a PCI4/750/ZRA potentiostat-galvanostat (Gamry Instrument) controlled by a computer, in a 3.5 wt% NaCl solution pH values of which is 5.76 at room temperature. The open circuit potential was measured after 60 min immersion of the tested samples with an active area of 0.283 cm² in the solution for potential stabilization. Potentiodynamic polarization measurements were made at a potential scan rate of 5 mV/s and the scanning range was set from –1 to +1 V.

2.3. Electroplating bath

The chemical composition of the plating bath and the operating conditions used to prepare electrodeposited Ni–B coatings are shown in Table II. H_3BO_3 amounts

*corresponding author; e-mail: akarabulut@sakarya.edu.tr

in the plating bath are 30, 60, 90, and 120 g/l for Ni-B, Ni-B2, Ni-B3, and Ni-B4 designations, respectively. Analytical reagents and distilled water were used to prepare the plating solution. Results of particle size measurement of unmilled and milled H_3BO_3 powders have been shown in Fig. 1a and b, respectively. Results showed that particle size (d_{50}) of H_3BO_3 powders reduced from 383.6 μm to 114.7 μm after the milling process.

TABLE II

Chemical composition of the plating bath and the operating conditions used to prepare electrodeposited Ni-B coatings.

Deposition parameter	Values
$NiSO_4$	24 g/l
$NiCl_2$	45 g/l
borondimethylamine	3 g/l
H_3BO_3	30, 60, 90 and 120 g/l
tallium	0.34 g/l
temperature	40–45 °C
pH	2–3
current density	21 mA/cm ²
magnetic stirring speed	900 rpm

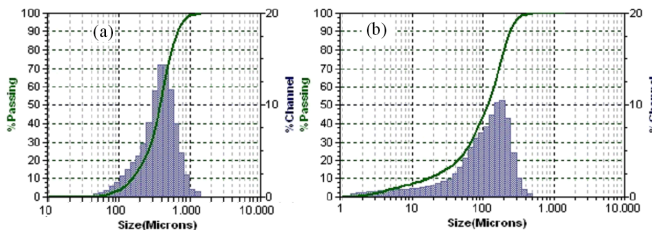


Fig. 1. Particle size measurements of H_3BO_3 powder: (a) unmilled, (b) 2 h planetary milled.

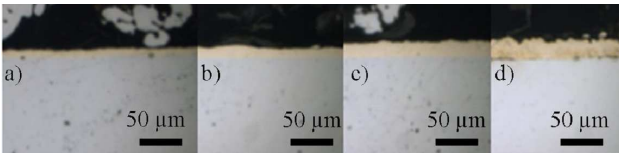


Fig. 2. Optical images of the cross-section of Ni-B coatings: (a) 30 g/l, (b) 60 g/l, (c) 90 g/l, (d) 120 g/l.

3. Results

3.1. Microstructure of the plating

Coating thickness increases as the amount of boric acid inside the solution increases along with the distance between the grains growing on the substrate (Fig. 2). The surface morphology of Ni-B coatings deposited from plating baths containing different amounts of H_3BO_3 is shown in Fig. 3a–g. H_3BO_3 amounts in the plating bath are 30 g/l for Ni-B (Fig. 3a,b), 60 g/l for Ni-B2 (Fig. 3c,d), 90 g/l for Ni-B3 (Fig. 3d,e) and 120 g/l for Ni-B4 (Fig. 3f,g).

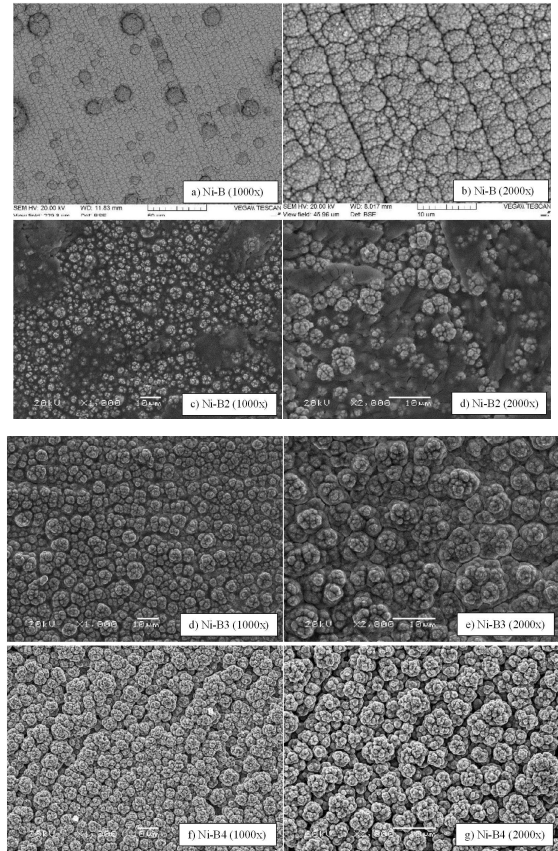


Fig. 3. SEM micrographs of the surface of the as-deposited Ni-B coatings: (a)–(b) Ni-B (30 g/l), (c)–(d) Ni-B2 (60 g/l), (d)–(e) Ni-B3 (90 g/l) and (f)–(g) Ni-B4 (120 g/l).

3.2. Phases and crystallinity analysis

In Fig. 4, XRD patterns of two samples are presented. Before the heat treatment, Fig. 4a indicates the amorphous phase without any other phases, such as nickel (Ni). After the heat treatment, amorphous phase crystallized and new phases have been formed. Peaks labeled “green”, “blue”, and “red” correspond to Ni_3B (ICDD File Card No. 73-1792), BNi_2 (ICDD File Card No. 48-1222), and nickel (ICDD File Card No. 04-0850), respectively.

3.3. Micro-hardness

Effect of heat treatment on the average microhardness value of electroplated Ni-B coatings is shown in Table III. Decreased powder size obtained by the milling process enabled better dispersion in solution and penetration into the coating.

3.4. Corrosion tests

Potentiodynamic polarization curves for Ni-B coatings with different boron additive are shown in Fig. 5. The values of different corrosion parameters calculated from Fig. 5 are also presented in Table IV for a clear comparison. It can be noticed that the further addition of boron

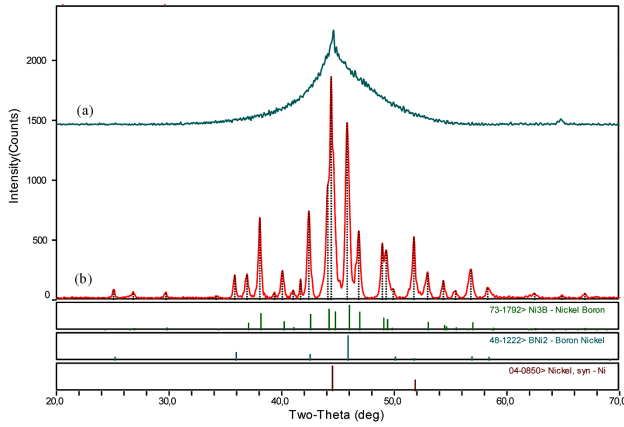


Fig. 4. XRD spectrum of Ni-B coating samples: (a) amorphous coating and (b) 400 °C heat-treated coating (NiB).

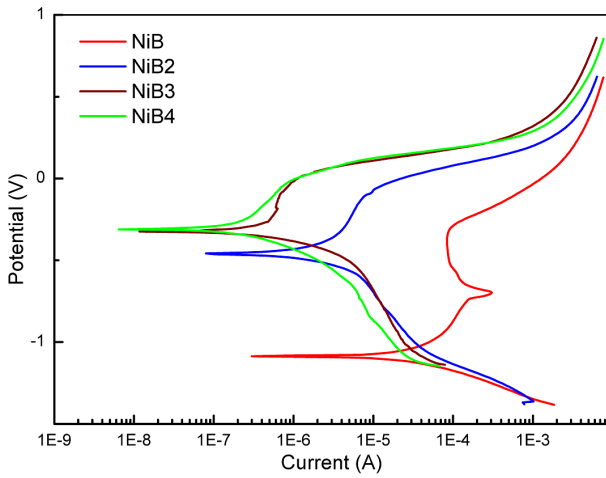


Fig. 5. Potentiodynamic polarization curves for the samples.

shifts the corrosion potential towards more positive value as compared to Ni-B coatings. Ni-B coating is so as the value of E_{corr} is less negative. The cathodic behavior of Ni-B coatings is better, although not yet clear and needs further investigation, as compared to Ni-B4 coatings. At this initial stage, it may be attributed to the formation of solid solution of boron with nickel at this composition which is more (less) cathodic than Ni-

TABLE III

Average micro hardness values before and after heat treatment.

Coating	Average HV _{0.005}		s.d.
	before	after	
Ni-B	590.3	1164.2	±68
Ni-B2	627.8	1179.4	±42
Ni-B3	687.1	1264.5	±54
Ni-B4	780.3	1386.2	±34

B4 (Ni-B) coatings. However, corrosion current density of Ni-B4 coatings is less compared to Ni-B coatings.

TABLE IV

Potentiodynamic test results. E_{corr} — corrosion potential; I_{corr} — corrosion current; β_A and B_C are Tafel slopes of the anodic and cathodic reactions.

Sample	E_{corr} [V]	I_{corr} [μ A]	β_A [$\times 10^{-3}$]	B_C [$\times 10^{-3}$]
Ni-B	-1.090	3.440	46.9	36.9
Ni-B2	-0.460	1.872	307.7	191.2
Ni-B3	-0.325	0.217	159.7	63.5
Ni-B4	-0.309	0.338	567.9	258.7

4. Conclusion

The microstructure dependence of hardening mechanism of as-deposited and heat-treated Ni-B alloys with varying boron content was investigated. H_3BO_3 has been intentionally added to the solution to promote grain growth. This cluster-like microstructure has maximum hardness of approximately 780.3 HV_{0.005}. Heat treatment at 400 °C for 1 h leads to the formation of Ni₃B and Ni₂B out of amorphous phase. With the increase of boron composition, the amount of Ni₃B phase increases which leads to higher obtained hardness up to 1386.2±34 HV_{0.005}. Similarly, corrosion resistance of the Ni-B coatings get better as the amount of boron in the plating bath increases.

References

- [1] L. Wang, Y. Gao, T. Xu, Q. Xue, *Appl. Surf. Sci.* **252**, 7361 (2006).
- [2] L. Wang, Y. Gao, Q. Xue, H. Liu, T. Xu, *Surf. Coat. Technol.* **200**, 3719 (2006).
- [3] B.N. Popov, *Development of Ni-Based High Wear Resistance Composite Coatings* Products Finishing, accessed: 14-Oct-2015.
- [4] Y. Liang, Y. Li, Q. Yu, Y. Zhang, W. Zhao, Z. Zeng, *Surf. Coat. Technol.* **264**, 80 (2015).
- [5] H. Huang, S. Chung, S. Pan, W. Tsai, C. Lin, *Surf. Coat. Technol.* **205**, 2097 (2010).
- [6] P. Indyka, E. Beltowska-Lehman, L. Tarkowski, A. Bigos, E. García-Lecina, *J. Alloys Comp.* **590**, 75 (2014).
- [7] F.J. He, Y.Z. Fang, S.J. Jin, *Wear* **311**, 14 (2014).
- [8] Z. Bangwei, H. Wangyu, Z. Qinglong, Q. Xuanyuan, *Mater. Character.* **37**, 119 (1996).
- [9] T. Watanabe, K. Suzuki, H. Kina, in: *212th ECS Meeting Abstracts MA2007-02*, Vol. 14, 2007.