

Characterization of pack borided AISI 4140 steel after nickel electroplating

S. Taktak*

Afyon Kocatepe University, Faculty of Technical Education, Department of Metal Education, 03200 Afyonkarahisar, Turkey

Received 21 August 2006, received in revised form 21 June 2007, accepted 21 June 2007

Abstract

A multilayer coating on AISI 4140 steel was obtained by combining nickel electroplating and pack boriding methods. Boriding treatment was carried out in Ekabor[®] II powders consisting of SiC on the steel precovered with nickel electroplating at the temperatures of 900 and 1000 °C for 3 and 6 h. X-ray diffraction analysis showed that on the sample borided at 900 °C, Ni₃₁Si₁₂, Ni₂Si, Ni₃B and Fe₂B phases formed, whereas on the samples borided at 1000 °C Fe₂B, Ni₅Si₂, Ni₇₄Si₂₆, Ni₂B and Ni₃B phases are present. It is probable that the formation of the nickel silicide layers was due to silicon in the boriding powder. The hardness of multilayer coatings was measured by using a Vickers indenter with a load of 100 g. Hardness measurements revealed that the hardness of multilayer coating was much higher than that of base steels. Hardness of nickel and silicon rich zones ranged between 700 and 900 HV, whereas hardness of iron, nickel and boron rich zones varied between 1400–1600 HV. Depending on boriding time and temperature the thickness of coating layers ranged from 51 to 165 μm. The best wear properties were obtained for the sample duplex treated at 1000 °C for 6 h. Corrosion tests showed that boriding at 900 and 1000 °C for 3 h followed by Ni electroplating improved the corrosion resistance.

Key words: nickel electroplating, pack boriding, silicides, wear, corrosion

1. Introduction

Electrochemical nickel deposition is one of the oldest protective-decorative metallic coatings for steels and nickel-plated steels are used in various industrial plants and equipment for their resistance to corrosion [1, 2]. With the increasing progress in engineering a growing need has been felt for materials that exhibit improved surface properties, such as an increased resistance to wear and corrosion. Use of plated steels in tribological applications is difficult due to its inferior wear resistance.

Boriding, on the other hand, is known to improve wear resistance since boron readily forms hard intermetallic compounds with many metals [3–6]. Boriding can be performed in numerous ways, including plasma, salt bath, paste and pack boriding techniques [7]. Boriding surface hardening treatment is appropriate for nickel metal because nickel can be easily borided and

the boride layer is thick. Boriding of nickel metal has been evaluated by a number of investigators. Ozbek et al. [8] and Ueda et al. [9] characterized the nickel that was borided into pack boriding medium with and without SiC powder and they observed Ni₅Si₂-Ni₂B and Ni₂B phases on the surface of nickel metal, respectively. Anthymidis et al. [10] reported that borided nickel in a fluidized bed reactor, containing B₄C-Al₂O₃ and activator, led to the formation of Ni₃B phase. Chen et al. [11] pointed out that during annealing above 450 °C, the nickel reacted with SiC to produce Ni₅Si₂, Ni₃Si and graphite precipitates.

Wierzchon et al. [12] and Sikorski et al. [13] have carried out plasma boriding on the surface of electrodeless nickel plated medium carbon steel. These works indicated that multicomponent boride layers consisting of Ni₄B₃, (Fe,Ni)B and (Fe,Ni)₂B have good resistance to frictional wear, a high hardness and a good corrosion resistance.

* Tel.: +90 272 2281311; fax: +90 272 2281319; e-mail address: taktak@aku.edu.tr

Table 1. Plating conditions for electrochemical nickel

Conditions	Value
Bath composition (g l^{-1})	NiSO ₄ : 200, NiCl ₂ : 25, HBO ₃ : 25 in H ₂ O
Temperature ($^{\circ}\text{C}$)	55
Current density (A dm^{-2})	4
pH	4
Time (min)	60
Plating thickness (μm)	45

Techniques of the electrochemical nickel deposition and pack boriding with SiC powder were combined for formation of the coatings that have a good combination of wear and corrosion properties. In this study, duplex treated, i.e. pack borided followed by nickel electroplating, AISI 4140 steel was characterized. Corrosion tests were performed by electrochemical method and wear behaviours were determined using ball-on-disc wear test.

2. Experimental details

2.1. Nickel electroplating and boriding

The substrate material, AISI 4140, essentially contained: 0.4 wt.% C, 0.86 wt.% Cr, 0.83 wt.% Mn, 0.29 wt.% Si, 0.18 wt.% Mo, 0.05 wt.% S and 0.016 wt.% P. The samples had a cylindrical shape and were 20 mm in diameter and 5 mm in length. AISI 4140 steel was electroplated by general purpose nickel plating bath containing nickel sulphate. Table 1 indicates operating conditions for nickel plating of 4140 steel.

Boriding was performed in a solid medium consisting of commercial Ekabor[®] II powders which had a nominal chemical composition of 90 % SiC, 5 % B₄C and 5 % KBF₄. Test materials to be borided were placed in contact with Ekabor[®] II powders and then transferred to an electrical resistance furnace. The test materials were heated to temperatures of 900 and 1000 $^{\circ}\text{C}$ under atmospheric pressure for 3 and 6 h duration time. This was followed by cooling in air.

Metallographic cross-sections were prepared to observe morphological details using BX60 Olympus optical microscope and LEO 1430 VP scanning electron microscope. XRD analysis was performed on the sample surface. Shimadzu XRD-6000 X-ray diffractometer, with a Cu K α radiation source of a wavelength of 0.15406 nm was employed for the characterization of the layers. The distributions of alloying elements from the surface to interior were recorded in linear scan by the X-ray spectroscopy (EDX). The thickness of the layers formed on AISI 4140 steel was measured by a

micrometer attached to the optical microscope. The hardness of the layers and substrates was measured on the cross-sections using a Shimadzu HMV-2 Vickers indenter with 100 g load. At least five indentations were made on each coating layer under each condition to check reproducibility of the hardness data.

2.2. Wear and corrosion tests

The wear resistance of samples was examined using a ball-on-disc test device at room temperature. The WC-Co ball with diameter of 4.6 mm was fixed and the disk sample was rotated at the speed of 0.3 m s^{-1} . Diameter of the worn track on the surface of the disc was about 6 mm. An applied load on the fixed ball was 10 N and total revolution was 8000 cycles for each test. Wear volume of the disk specimen was determined from the cross-sectional area of the wear track using a surface profilometer.

Electrochemical polarization experiments were performed using a potentiostat in 1 N H₂SO₄ solution at a temperature of 298 K. The electrodes were prepared by connecting a wire to one side of the samples that was covered with teflon. One side of the specimen with an area of approximately 20 mm^2 was exposed to the solution. The electrochemical cell consists of the specimens as the working electrode, a saturated calomel reference electrode, and a platinum counter electrode. The specimens were immersed in the test solution, and a polarization scan was carried out towards more noble values at a rate of 2 mV s^{-1} , after allowing a steady state potential to develop.

3. Results and discussion

Figure 1 shows optical micrograph of electroplated nickel layer with about 45 μm thickness on the 4140

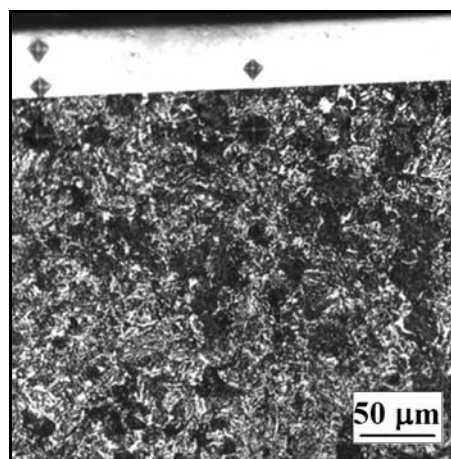


Fig. 1. Optical micrograph of electroplated nickel layer on the 4140 steel.

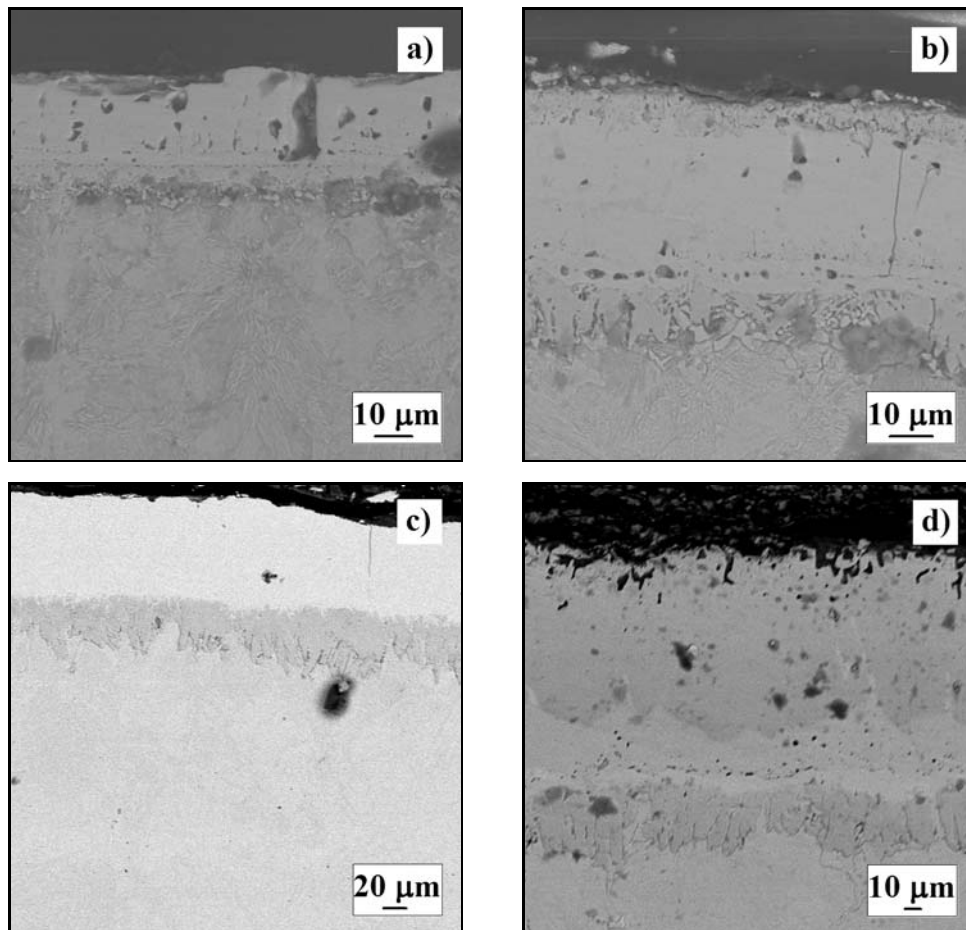


Fig. 2. SEM micrograph of pre-covered with nickel and pack borided at: a) 900 °C for 3 h, b) 900 °C for 6 h, c) 1000 °C for 3 h, and d) 1000 °C for 6 h.

steel. The core microstructure of 4140 steel before boriding process is composed of pearlite and ferrite. Figure 2 shows SEM microstructure of duplex treated 4140 steel, i.e. borided at temperatures of 900 and 1000 °C for 3 and 6 h after nickel electroplating. SEM cross-sectional examinations show two distinct layers at 900 °C and 1000 °C for 3 h. However, more than two distinct layers are found at 900 °C and 1000 °C for 6 h. As seen in Fig. 2, nickel and silicon-rich zones have relatively flat morphology when compared with the iron boride layers having a columnar morphology.

The X-ray diffraction patterns of duplex treated at 900 and 1000 °C for 3 and 6 h are given in Fig. 3. The presence phases of the layer borided at 900 °C for 3 h are $\text{Ni}_{31}\text{Si}_{12}$, Ni_3B and Fe_2B . Increasing the boriding time up to 6 h results in increase of silicon concentration and Ni_2Si , Ni_3B and Fe_2B phases are found at this temperature and time. For boriding temperature of 1000 °C and holding time of 3 h, XRD pattern shows Ni_5Si_2 , $\text{Ni}_{74}\text{Si}_{26}$, Ni_2B and Ni_3B phases. However, XRD pattern indicates alone Fe_2B phase with increasing the boriding time up to 6 h at 1000 °C. At this temperature and time, phases in the second and third layers could not be observed because the near-

-surface layer is considerably thick. Further X-ray diffraction analysis is needed to confirm other nickel silicides and borides phases. For this, near-surface layer is ground to remove layer thickness of 80 μm from the top. The last XRD analysis shows Ni_5Si_2 , Ni_2B and Fe_2B phases.

XRD studies indicate that silicon, which comes from boriding powder, introduces into nickel electroplating and forms nickel silicides. As a matter of fact, the diffusivity of silicon and boron atoms modifies the electrochemical nickel coating. Previous studies done by Palombarini et al. [14] reveal that the SiO_2 component being in the boronizing powder is able to give rise to a siliciding gaseous compound, which generally is assumed to be SiF_4 . These gaseous products react with nickel plating. Ohi et al. [15] reported that in Ni/SiC system, Ni reacts with SiC to form nickel silicides and carbon. Generally, Ni_2Si is the dominant species in a large temperature range between 600 and 950 °C. Some papers on Ni/SiC reactions also claim the existence of $\text{Ni}_{31}\text{Si}_{12}$ at the surface or NiSi at the interface [16, 17]. In fact, Ni_5Si_2 , $\text{Ni}_{74}\text{Si}_{26}$ and $\text{Ni}_{31}\text{Si}_{12}$ phases are unstable nickel silicides phases according to the Ni-Si phase diagram [18]. Gay and Quakernaat

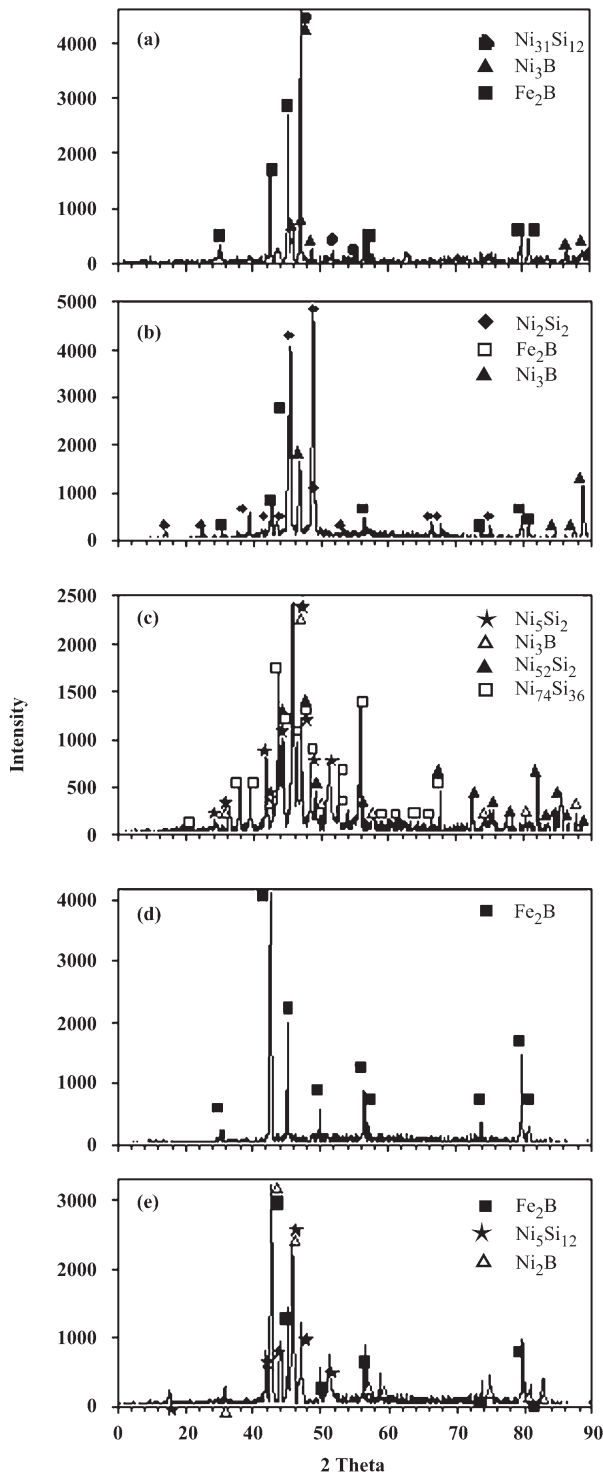


Fig. 3. X-ray diffraction patterns observed from the surface of the 4140 steel which was pre-covered with Ni and borided at: a) 900 °C for 3 h, b) 900 °C for 6 h, c) 1000 °C for 3 h, d) 1000 °C for 6 h, and e) X-ray of sample in (d) after the boride layer is ground about 80 μm from the top.

[19] pointed out that in the initial stage of layer growth of the nickel silicides, unstable nickel silicides phases

Table 2. Concentration of elements (wt.%) in selected micro-regions of coating layer formed by boriding at 1000 °C for 6 h on 4140 steel pre-covered with nickel

Point	Concentration of elements (wt.%)			
	Fe	Ni	Si	Cr
A	92.64	5.99	–	1.37
B	59.33	31	9.67	–
C	98.65	–	–	1.35

can be formed and after annealing, these phases were completely transformed into the stable nickel silicide phases. However, Van Dyck et al. [20] reported that additions of Cr and B into nickel silicides promoted the formation of unstable nickel silicides such as $\text{Ni}_{31}\text{Si}_{12}$.

The distribution of elements from surface to interior was determined using EDX line analysis. Figure 4 shows the distribution of Fe, Ni and Si elements from surface to interior at the distances of 80–200 μm at temperatures of 900 and 1000 °C for 3 and 6 h duration. XRD findings are confirmed by EDX line analysis. As seen in Fig. 4a and b, silicon concentrates in coating layer and silicon and nickel concentrations are higher than iron concentration. At about distance of 30–35 μm from surface, nickel and silicon concentrations in coating layer drop whereas iron concentration abruptly increases. With increasing boriding temperature, the diffusion depth of nickel and silicon increases (Fig. 4c). Contrary to boriding at 900 °C, silicon concentration in the coating layer is lower than iron concentration. This shows that iron diffuses into the coating layer. The concentrations of nickel and silicon on the surface sharply decrease at about 90 μm distance from surface whereas iron concentration sharply increases. With increasing boriding time at temperature of 1000 °C, the diffusion of iron increases on the surface. Figure 4d indicates that concentration of iron is higher than both nickel and silicon concentrations at each layer. For detailed investigation, EDX point analysis was carried out on the surface of sample pre-covered with nickel and borided at 1000 °C for 6 h. EDX spectra and concentration of elements (wt.%) at each point are shown in Fig. 5 and Table 2, respectively. As seen in Fig. 5 and Table 2, silicon concentrates only in the B point and this zone contains about 9.67 wt.% of Si. However, nickel concentrates in the near-surface zones (A and B points). The near-surface zone (A point) includes about 6 wt.% Ni whereas next zone (B point) includes about 31 wt.% Ni. No nickel is found in the iron boride needles (C point).

At 900 °C for 3 h, the first layer, about 37 μm thick, is composed of $\text{Ni}_{31}\text{Si}_{12}$ and Ni_3B phases. At this temperature EDX line analysis indicates that an amount of iron diffuses into the coating. Below the

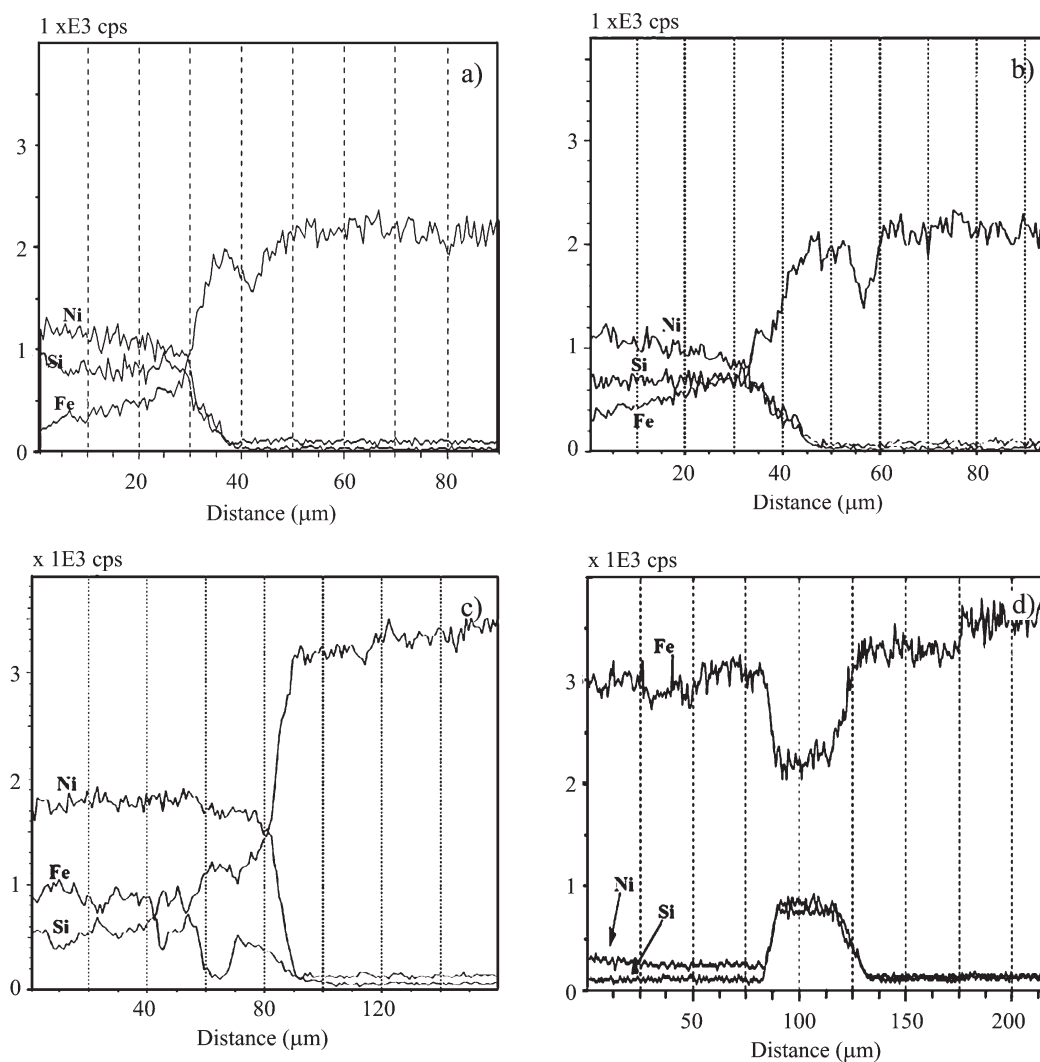


Fig. 4. EDX line analysis along the cross-sections of 4140 steel pre-covered with Ni electroplate and borided at: a) 900 °C for 3 h, b) 900 °C for 6 h, c) 1000 °C for 3 h, and d) 1000 °C for 6 h.

first layer, the needle-shaped zone, about 14 μm thick, is composed of Fe_2B phase. At 900 °C for 6 h, the near-surface layer, about 48 μm thick, is composed of Ni_2Si and Ni_3B phases. Nickel boride can form as thin zone at the outer surface because silicon is not soluble in boride phases [7] and silicon rich zone can concentrate strongly beneath this zone. The needle-shaped Fe_2B zone, about 16 μm thick, extends down much below the boundary of the first layer. When the system is heated to temperature of 1000 °C, iron and nickel diffuse mutually into one another so that it is the Fe-Ni solid solution, which is subjected to boriding. This process affects in a decisive way the phase composition and the structure of the borided layer. The near-surface layer, about 90 μm thick, contains Ni_5Si_2 , $\text{Ni}_{74}\text{Si}_{26}$, Ni_2B and Ni_3B phases. Below this layer, iron boride zone is found. The needles of this boride phase penetrate into the substrate to a depth of up to about 50 μm from the first layer. For borid-

ing at 1000 °C for 6 h three layers are found. During the boriding process, the diffusion of iron increases towards the surface of sample, while nickel and especially silicon are pushed into the interior of the coating and Ni and Si concentrate within medium zone of the coating layer. However, the concentration of iron at all layers is higher than that of nickel and silicon (see Table 2). EDX analyses suggest that the near-surface layer, about 85 μm thick, is composed of $(\text{Fe},\text{Ni})_2\text{B}$ phase, i.e. nickel is dissolved in the iron boride lattice. The second layer, about 40 μm thick, contains Ni_5Si_2 and Ni_2B phases. The third zone, about 40 μm thick, is composed of Fe_2B needles penetrating the substrate and, thus, improves the adhesion of the layer.

Figure 6 shows the hardness variation of the Ni plated and then borided 4140 steel at 900 and 1000 °C from the surface into the matrix. As seen in Fig. 6a, hardness of the layer that is located near the surface is about 900 $\text{HV}_{0.1}$ for boriding time of 3 and 6 h.

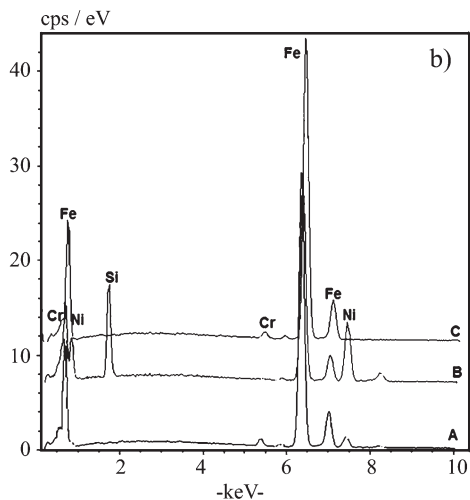
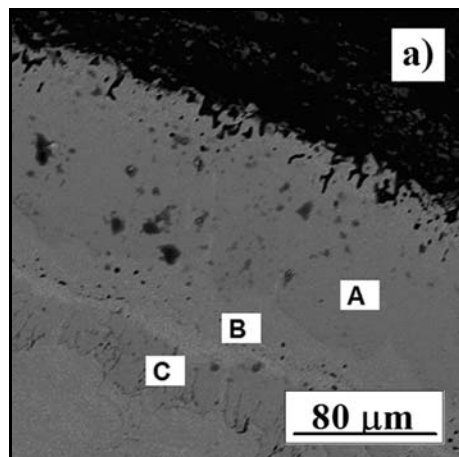


Fig. 5. a) SEM micrograph and b) EDX spectra of illustrated points with A, B and C letters on the SEM photos for the samples borided at 1000°C for 6 h.

However below the near-surface zone, hardness values abruptly increase up to 1435 and 1580 HV for 3 and 6 h, respectively, due to the presence of needle-shaped Fe₂B phase and then decrease to matrix hardness. Figure 6b indicates that hardness values of exterior layers are different for the samples borided at 1000°C for 3 and 6 h. For boriding time of 3 h, hardness varies between 945 and 732 HV at exterior layer and then increases up to 1640 HV. For boriding of 6 h, there are three different hardness layers (Fig. 7). At layer located near the surface, hardness ranges between 1345 and 1310 HV. Below the near-surface zone, hardness is about 800 HV and beneath, it also is about 1580 HV.

The differences in the hardness of layers may be explained as the consequence of the presence of complex phases formed at 900 and 1000°C treatments in the coating layer. Generally, layers have two different hardness values. Hardness of nickel and silicon rich zones ranges between 700 and 900 HV. Wang et al.

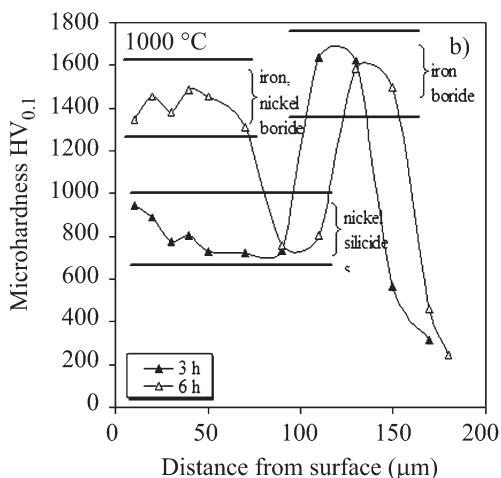
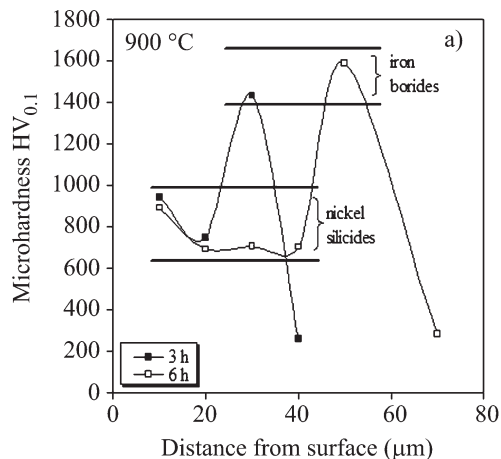


Fig. 6. Hardness variation of the nickel plated and borided 4140 steel at: a) 900°C and b) 1000°C from the surface into the matrix.

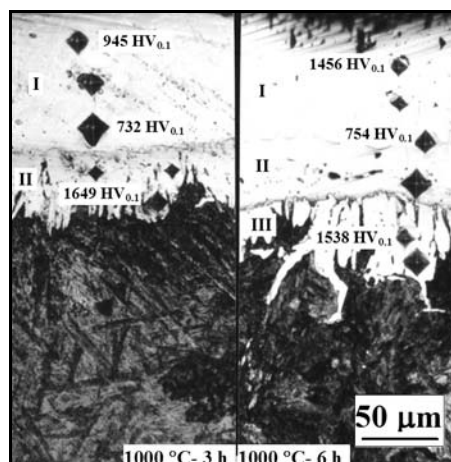


Fig. 7. Optical micrograph of the samples borided at 1000°C for 3 and 6 h showing Vickers indentation marks.

[21] have reported that hardness of Ni₂Si/NiSi coating formed on steel was about 800 HV. Iron and boron

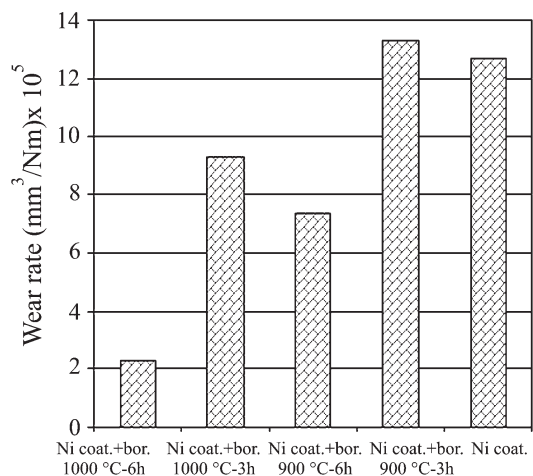


Fig. 8. The wear rates of Ni-coated and duplex treated steel samples.

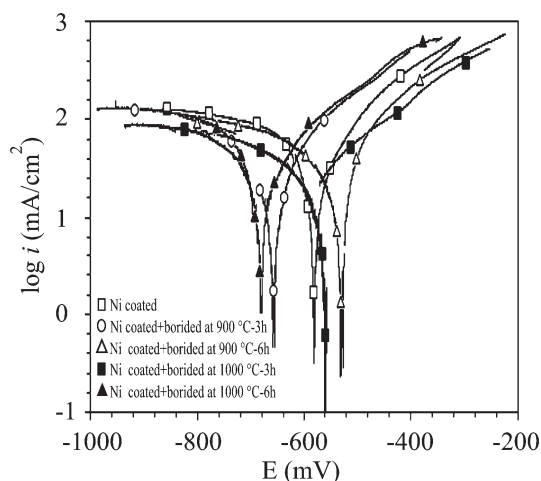


Fig. 9. Anodic polarization curves of Ni-coated and duplex treated steel samples in 1 N H₂SO₄ solution.

can affect the hardness of this layer. But it is difficult to clarify the effect of these elements on this layer, so it is not discussed here. However, hardness of iron, nickel and boron rich zones varies between 1400–1600 HV. This is in agreement with previous studies [3, 7, 22].

Figure 8 shows the wear rates of Ni coated and then borided steel samples. It is evident that the wear rates of the duplex treated samples improved for temperature and time. When comparing the wear resistance of duplex treated steels, the best wear properties were obtained for the sample duplex treated at 1000 °C for 6 h. The wear rate of the sample treated at 1000 °C for 6 h is low by a factor of 5.6 compared with only Ni coated sample and by a factor of 5.9 compared with the sample duplex treated at 900 °C for 3 h. This could be probably due to high wear resistance of hard iron

borides [7]. The worse wear properties were obtained for the samples duplex treated at 900 °C for 3 h and only Ni electroplated. This may be attributed to soft nickel and nickel silicide layer.

Anodic polarization curves for duplex treated samples, recorded after immersion in the corrosive 1 N H₂SO₄ solution, are shown in Fig. 9. The pack boriding containing SiC powder changed the polarization properties of Ni electroplated 4140 steel. The samples, borided at 900 and 1000 °C for 3 h followed by Ni coating, exhibit higher corrosion potential (–530 and –560 mV) and lower corrosion current density (31.6 and 38 mA cm^{–2}) in comparison with only Ni coated steels (–580 mV and 39.8 mA cm^{–2}). This appears to be due to the formation of nickel silicides at the outermost surface. However, the samples, borided at 900 and 1000 °C for 6 h followed by Ni coating, show lower corrosion potential (–660 and –680 mV) and higher corrosion current density (41.7 and 45.7 mA cm^{–2}) in comparison with only Ni coated steels. This may be attributed to iron diffusion through outermost surface due to long treatment time. It is clear that duplex treating for 3 h improves the corrosion resistance. These results are in agreement with literature. Wang et al. [21] showed that Ni-Si coatings in 0.5 N H₂SO₄ solutions are considerably more corrosion resistant than austenitic stainless steel. In addition, it was reported that the high silicon content of intermetallics provided a good corrosion and oxidation resistance owing to the formation of a protective silica film [23].

5. Conclusions

In this study, the structure and hardness of multilayer coatings on AISI 4140 steel obtained by combining nickel electroplating and pack boriding methods were investigated. Following conclusions can be drawn from the results:

- When AISI 4140 steel, pre-covered with electrochemical nickel plating, is subjected to pack boriding, containing SiC powder, a multicomponent surface layers form on it. Nickel and silicon rich zones have a flat and smooth morphology, whereas iron boride layers have a columnar structure and they extend down much below the boundary of the deposited nickel electroplating.

- X-ray diffraction analysis showed that at low boriding temperature, Ni₃₁Si₁₂, Ni₂Si, Ni₃B and Fe₂B phases formed, whereas on the samples borided at high temperature Ni₅Si₂, Ni₇₄Si₂₆, Ni₂B, Ni₃B, Fe₂B and (Fe,Ni)₂B phases are present.

- Hardness of nickel and silicon rich zones ranges between 700–900 HV, whereas hardness of iron and boron rich zones varies between 1400–1600 HV.

- The best wear properties were obtained for the

sample duplex treated at 1000 °C for 6 h. The wear rate of the sample treated at 1000 °C for 6 h is low by a factor of 5.6 compared with only Ni coated sample. Boriding of nickel-plated steels enhanced the surface hardness and wear resistance.

– Boriding of nickel-plated steels for 3 h improved the corrosion resistance compared with only Ni coated sample.

Acknowledgements

The authors express their thanks to TUAM of A. K. University of Turkey for allowing them to perform the Energy Dispersive X-ray spectroscopy EDX analysis. Special appreciations are extended to Ass. Prof. A. Buyuksagis of A. K. University for help with the corrosion tests.

References

- [1] RUBINSTEIN, M.—PENROSE, R. M.: Surf. Coat. Technol., 36, 1988, p. 847.
- [2] GIANELOS, L.—Mc MULLEN, W. H.: Nickel Plating. In: ASM Int. Handbook. Materials Park, OH, 5, 1991, p. 199.
- [3] CARBUCICCHIO, M.—PALOMBARINI, G. P.: J. Mater. Sci. Lett., 6, 1987 p. 1147.
- [4] MELENDEZ, E.—COMPAS, I.—ROCHA, E.—BARRON, M. A.: Mater. Sci. Eng. A, 234–236, 1997, p. 900.
- [5] USTA, M.: Surf. Coat. Technol., 194, 2005, p. 251.
- [6] USTA, M.—OZBEK, I.—IPEK, M.—BINDAL, C.—UCISIK, A. H.: Surf. Coat. Technol., 194, 2005, p. 330.
- [7] SINHA, A. K.: Boriding (boronizing). In: ASM Int. Handbook. Materials Park, OH, USA, 4, 1991, p. 437.
- [8] OZBEK, I.—AKBULUT, H.—ZEYDIN, S.—BINDAL, C.—UCISIK, A. H.: Surf. Coat. Technol., 126, 2000, p. 166.
- [9] UEDA, N.—MIZUKOSHI T.—DEMIZU, K.—SONE, T.—IKENAGA, A.—KAWAMOTO, M.: Surf. Coat. Technol., 126, 2000, p. 25.
- [10] ANTHYMIDIS, K. G.—ZINOVIADIS, P.—ROUSOS, R.—TSIPAS, D. N.: Mater. Res. Bull., 37, 2002, p. 515.
- [11] CHEN, C. K.—FENG, H. M.—LIN, H. C.—HON, M. H.: Thin Solid Films, 416, 2002, p. 31.
- [12] WIERZCHO, T.—BIELISKI, P.—SIKORSKI, K.: Surf. Coat. Technol., 73, 1995, p. 121.
- [13] SIKORSKI, K.—WIERZCHO, T.—BIELISKI, P.: J. Mater. Sci., 33, 1998, p. 811.
- [14] PALOMBARINI, G.—CARBUCICCHIO, M.: J. Mater. Sci. Lett., 12, 1993, p. 797.
- [15] OHI, A.—LABIS, J.—MORIKAWA, Y.—FUJIKI, T.—HIRAI, M.—KUSAKA, M.—IWAMI, M.: Appl. Surf. Sci., 190, 2002, p. 366.
- [16] BACHLI, A.—NICOLET, M. A.—BAUD, L.—JAUSAUD, C.—MADAR, R.: Mater. Sci. Eng. B, 56, 1998, p. 11.
- [17] HAN, S. Y.—SHIN, J. Y.—LEE, B. T.—LEE, J. L.: J. Vac. Sci. Technol. B, 20, 2002, p. 1496.
- [18] ASM Int. Handbook, Phase Diagrams. Ed.: Baker, H. Materials Park, OH, 3, 1992, p. 318.
- [19] GAY, A. J.—QUAKERNAAT, J.: J. Less-Common Metals, 40, 1975, p. 21.
- [20] VAN DYCK, S.—DELAEY, L.—FROYEN, L.—BUEKENHOUT, L.: Mater. Charact., 38, 1997, p. 1.
- [21] WANG, H. M.—WANG, C. M.—CAI, L. X.: Surf. Coat. Technol., 168, 2003, p. 202.
- [22] BINDAL, C.—UCISIK, A. H.: Surf. Coat. Technol., 122, 1999, p. 208.
- [23] ULVENSOEN, J. H.—RORVIK, G.—KYVIK, T.—PETTERSEN, K.—L'ESTRADE, L.: In: Proceedings Int. Symp. on Structural Intermetallics. Ed.: Darolia, R. et al. Warrendale, PA, TMS 1993, p. 707.