

Effect of post-oxidizing on tribological and corrosion behaviour of plasma nitrocarburized AISI 4140 steel

M. Karakan^{1*}, Ö. Denктаş²

¹Department of Mechanical Engineering, Ataturk University, 25240 Erzurum, Turkey

²Aşkale College of Vocational, Ataturk University, 25240 Erzurum, Turkey

Received 9 February 2009, received in revised form 5 June 2009, accepted 5 June 2009

Abstract

AISI 4140 steel was initially plasma nitrocarburized at 570 and 700°C for 4 h in a gas mixture of 60 % N₂ + 37 % H₂ + 3 % CO₂. After nitrocarburizing, post-oxidation treatment was performed at 450°C for 1 h using oxidation gas mixture ratios of 50 % H₂ + 50 % O₂ and pure oxygen. The structural, mechanical, tribological, and corrosion properties of nitrocarburized and post-oxidized steel were analysed using an X-ray diffraction, microhardness tester, scanning electron microscopy, pin-on-disc tribotester, and electrochemical polarization. The experimental results showed that oxide layer included Fe₂O₃ and Fe₃O₄ phases while the compound layer formed after both ferritic and austenitic nitrocarburizing consisted of Fe₂₋₃(N,C) and Fe₄(N,C) phases. Post-oxidation treatment improved further tribological and corrosion properties in consequence of nitrocarburizing. The contribution of post-oxidation treatment made after the ferritic nitrocarburizing was much more than the contribution of post-oxidation treatment made after the austenitic nitrocarburizing. Furthermore, it was seen that using hydrogen in oxidation gas mixture had useful effects such as better tribological properties and corrosion resistance.

Key words: plasma nitrocarburizing, post-oxidizing, tribology, corrosion

1. Introduction

With developing technology, material properties required have changed according to using areas and conditions with increasing variety and demand. For meeting those inclinations, the interest to surface treatment techniques consisting of changing the only surface part instead of the whole of the material has increased rapidly in the last years. There are a lot of surface treatment techniques applied to the materials to increase their surface hardness, wear resistance, corrosion resistance, and fatigue strength. Nitrocarburizing which has showed great development in the last twenty years is a thermochemical treatment technique including the diffusion of carbon and nitrogen atoms to material surface at the same time [1–6].

Nitrocarburizing can be applied at the conditions of solid, liquid and gas. The usage in the industry of the nitrocarburizing treatment applied at the plasma conditions in respect of the other known techniques

has increased gradually in the last years. The nitrocarburizing treatment applied at the plasma conditions has a lot of advantages: it is environmentally friendly, its operation cost is low, the sensitive control of the treatment parameters is possible and after treatment, the structures with more superior technical properties can be obtained [1, 7].

Because the compound layer formed during nitrocarburizing treatment is porous, the corrosion resistance of the material could not have been improved enough. To improve corrosion properties and increase the assistance of the treatment to the tribological properties, post-oxidation treatment based on the forming of oxide layer on the surface has been started to investigate rapidly for last five years. Studies on the structure, the growing kinetics and the effects on the material properties of the oxide film have been at the beginning stage yet, and the studies include a lot of subjects which need an investigation, like the aid of oxide film on

*Corresponding author: tel.: +90 442 231 48 42; fax: +90 442 236 09 57; e-mail address: mkarakan@atauni.edu.tr

the treatment parameters and material properties [8–16].

Plasma nitrocarburizing treatment is classified into two groups as ferritic and austenitic according to process temperature. While treatment realized under eutectic point (592 °C) at Fe-N diagram is named as ferritic nitrocarburizing, the treatment over this temperature is called austenitic nitrocarburizing [17, 18]. The aim of the present research is to evaluate the effect of the nitrocarburizing condition and gas mixture on post-oxidation. The study includes the nitrocarburizing in the plasma atmosphere at the ferritic and austenitic conditions of AISI 4140 steel materials, the oxidizing of the specimens at the different plasma atmosphere, and the investigation of the effect of the treatments on the corrosion resistance and tribological properties using various techniques and analysis.

2. Experimental details

An AISI 4140 low-alloy steel, whose chemical compositions are given in Table 1, was used in the experimental studies. The specimens were normalized initially at 850 °C for 30 minutes, and then cooled in air. Plasma nitrocarburizing and post-oxidizing were carried out in the same equipment which was developed by Çelik et al. [19]. After cleaning with alcohol, the specimens were placed into the chamber, which was evacuated to 2.5 Pa. Prior to the processes, the specimens were subjected to cleaning by hydrogen sputtering for 15 minutes under a voltage of 500 V and a pressure of 500 Pa to remove surface contaminations. Then, the specimens were initially plasma nitrocarburized at 570 (ferritic) and 700 °C (austenitic) for 4 h in a gas mixture of 60 % N₂ + 37 % H₂ + 3 % CO₂. After nitrocarburizing, post-oxidation treatment was performed at 450 °C for 1 h using oxidation gas mixture ratios of 50 % H₂ + 50 % O₂ and pure oxygen under a constant pressure of 200 Pa. This process is particularly attractive, since it allows both plasma nitrocarburizing and post-oxidizing treatments in a single operation, simply by varying the treatment atmosphere and the working conditions.

A Rigaku diffractometer was used to analyse the structure of the compound and oxide layers. The X-ray diffractometer was operated at 30 kV and 30 mA with Cu K α radiation. After plasma nitrocarburizing and post-oxidizing, the thin compound and oxide layers formed on the surface were removed by polishing prior to metallographic examination and microhardness testing. The diffusion layer and the maximum surface hardness were measured by using a Buehler Omnimet MHT1600-4980T instrument at a constant load of 50 gf and a loading time of 15 s. The maximum surface hardness at 25 μ m depth was chosen for comparison so that any possible effects from

Table 1. Chemical composition of AISI 4140 steel (wt.%)

C	Mn	Si	Cr	Ni	Mo	W	S	Cu	P
0.36	0.80	0.30	0.85	0.07	0.075	0.034	0.005	0.143	0.014

a compound layer would be negligible. Wear tests were carried out on Teer POD-2 pin-on-disc tester using a 5 mm diameter tungsten carbide-cobalt ball as the pin. The friction force was monitored continuously by means of a force transducer. Unlubricated wear tests with a sliding distance of 141 m were conducted at room temperature, a relative humidity of approximately 50 %, a sliding speed of 4.7 m min⁻¹, normal load of 10 N and a wear track diameter of 10 mm. The samples were weighted at precision balance before and after wear test and the weight loss was determined, and this value was used in wear rate calculation. Additionally, the wear volume was calculated from the superimposed profiles to correct wear rate calculation. The worn regions after the wear tests were examined by using a Jeol 6400 SEM. Electrochemical polarization experiments were performed using a potentiostat, Potentioscan Wenking POS 73. The electrodes were prepared by connecting a wire to one side of the sample that was covered with cold setting resin. One side of the specimen with an area of approximately 1 cm² was exposed to the solution. The polarization measurements were carried out in a corrosion cell containing 3.5 % NaCl solution of 500 ml. 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 1 mV s⁻¹, after allowing a steady state potential to develop.

3. Results and discussion

Figure 1 shows an SEM micrograph of post-oxidized AISI 4140 steel after ferritic nitrocarburizing. An oxide layer covering surface overall was formed after plasma nitrocarburizing on compound layer consisting of Fe₂₋₃(N,C) and Fe₄(N,C) phases. It was observed from the XRD analyses given in Fig. 2 that the oxide layer with 0.5–2 μ m thickness consists of magnetite and hematite phases depending on the parameter of oxidation treatment. Because the compound layer with pores was formed in consequence of nitrocarburizing [18, 20], the corrosion properties affected negatively were improved owing to closing of these pores. Although this situation reduces the surface roughness a little, as seen in Table 2, it also con-

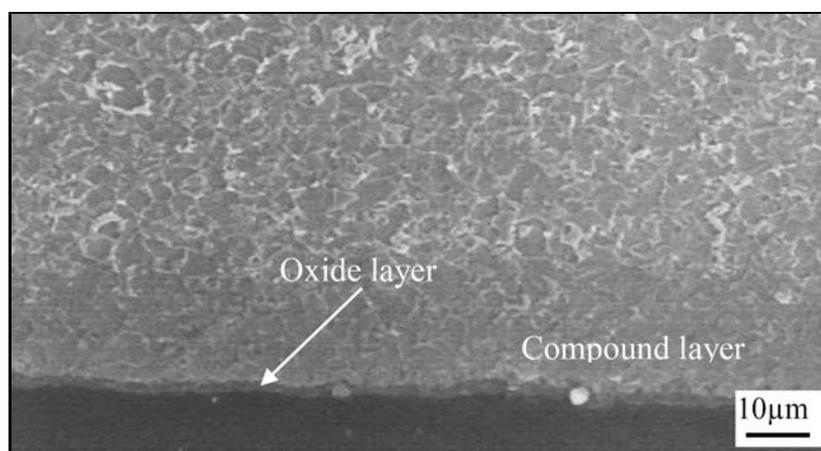


Fig. 1. SEM micrograph of post-oxidized AISI 4140 steel after ferritic nitrocarburizing.

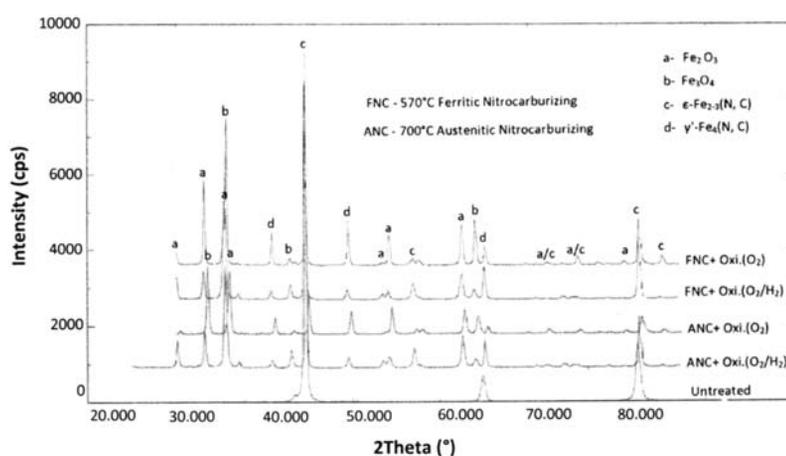


Fig. 2. XRD result for nitrocarburized + post-oxidized AISI 4140 steel.

Table 2. Experimental results obtained after plasma nitrocarburizing and post-oxidizing of AISI 4140 steel

Process	Experimental results					
	Surface hardness HV _{0.05}	Compound layer (μm)	Oxide layer (μm)	Diffusion layer (μm)	Surface roughness <i>Ra</i>	Friction coefficient
Ferritic nitrocarburizing	530–570	15–19		210–230	0.27–0.35	0.27–0.31
FNC + oxidizing (O ₂)	470–510		0.5–2		0.11–0.21	0.24–0.26
FNC + oxidizing (O ₂ /H ₂)	470–510		0.5–1.5		0.18–0.25	0.23–0.25
Austenitic nitrocarburizing	520–560	16–20		240–270	0.27–0.37	0.25–0.28
ANC + oxidizing (O ₂)	450–490		0.5–2		0.17–0.21	0.24–0.26
ANC + oxidizing (O ₂ /H ₂)	450–490		0.5–1.5		0.22–0.26	0.23–0.26
Untreated	321				0.01–0.05	0.29–0.33

tributes to tribological and corrosion properties positively.

XRD results of plasma nitrocarburized + post oxidized AISI 4140 steel are shown in Fig. 2. Figure 2 demonstrates that the microstructure consists of Fe_{2–3}(N,C) and Fe₄(N,C) phases formed as a result of nitrocarburizing, and magnetite (Fe₃O₄) and hematite

(Fe₂O₃) phases formed in consequence of post oxidation. The compound layer, which especially includes dense ϵ phase, occurred due to both ferritic and austenitic plasma nitrocarburizing. This layer is almost single phase and more dense in austenitic condition. Since the compound layer is single phase, the abrasive particles are reduced. The positive contribution of

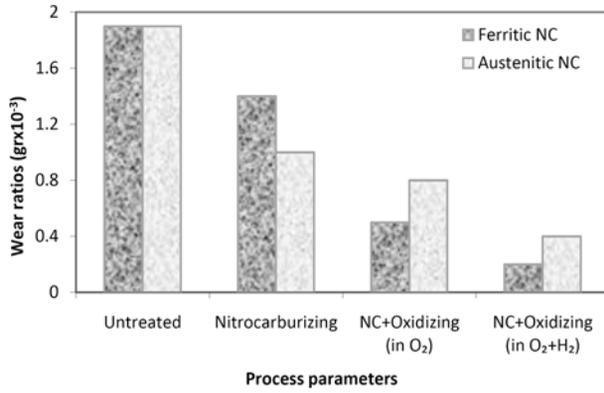


Fig. 3. Effect of process parameters on wear rate.

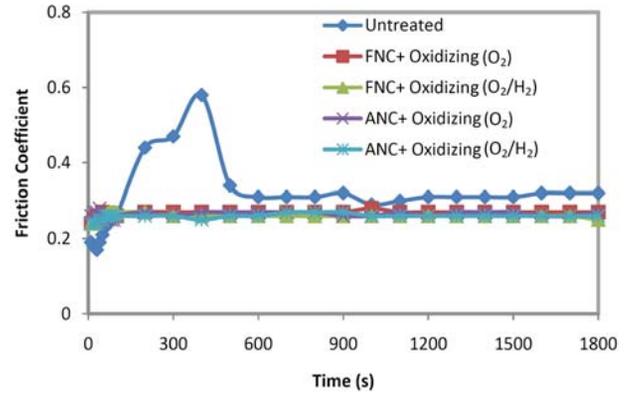


Fig. 6. The variation between friction coefficient and time for nitrocarbured + post-oxidized AISI 4140 steel.

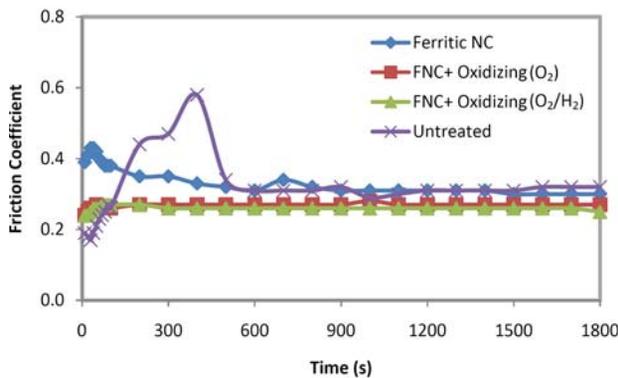


Fig. 4. The variation between friction coefficient and time for ferritic nitrocarbured and post-oxidized AISI 4140 steel.

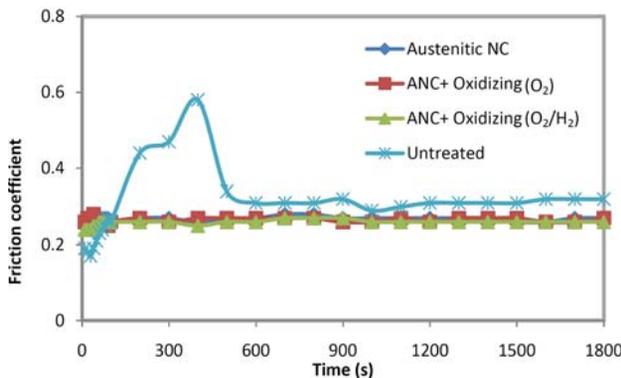


Fig. 5. The variation between friction coefficient and time for austenitic nitrocarbured and post-oxidized AISI 4140 steel.

this situation, which causes a reduction of abrasive particles, is shown in related figures. However, an oxide layer covering the surface of the compound layer occurs after oxidation treatment. The contribution of this layer consisting of Fe₃O₄ and Fe₂O₃ phases to tri-

bological properties and corrosion resistance is shown in figures.

As shown in Fig. 3, the wear rate of both nitrocarbured and post-oxidized samples was reduced when compared to untreated samples. Adhesive and abrasive wear modes were observed for the nitrocarbured samples. It attracted attention that the abrasive particles caused by decomposition of hard and brittle compound layer including two different phases (ϵ and γ) after process increased wear. Such a nitrocarbured phase structure is known to be detrimental to the tribological properties, particularly under impact loading conditions, due to the inherently high internal stresses arising from the phase boundaries. Therefore, the primary aim of nitrocarburing is to produce a compound layer composed predominantly of a single ϵ -phase, which has an hcp structure and offers superior resistance to seizure, score and scuffing [7]. Less wear for austenitic nitrocarbured samples was observed as compared to ferritic nitrocarbured samples, because the amount of abrasive particles was reduced due to partly single phase (ϵ) compound layer in austenitic conditions. Besides, the oxidation treatments after nitrocarburing caused a significant reduction in wear rate. The reduction of the wear rate was more intensive when atmosphere with hydrogen was used according to that of pure oxygen atmosphere. This can be attributed to more dense magnetite phase in the hydrogen atmospheres. It is noted that the oxidation treatments after ferritic treatments have more evident effect compared to that of austenitic conditions. This is owing to low particle hardness that resulted in oxidation, and thus reduction in abrasive effect. The lowest wear rate was obtained for the oxidation condition applied in hydrogen including atmosphere after ferritic nitrocarburing.

Figures 4, 5 and 6 show the change of friction coefficients during pin-on-disc tests. The treatments carried out under all the conditions demonstrate that a little

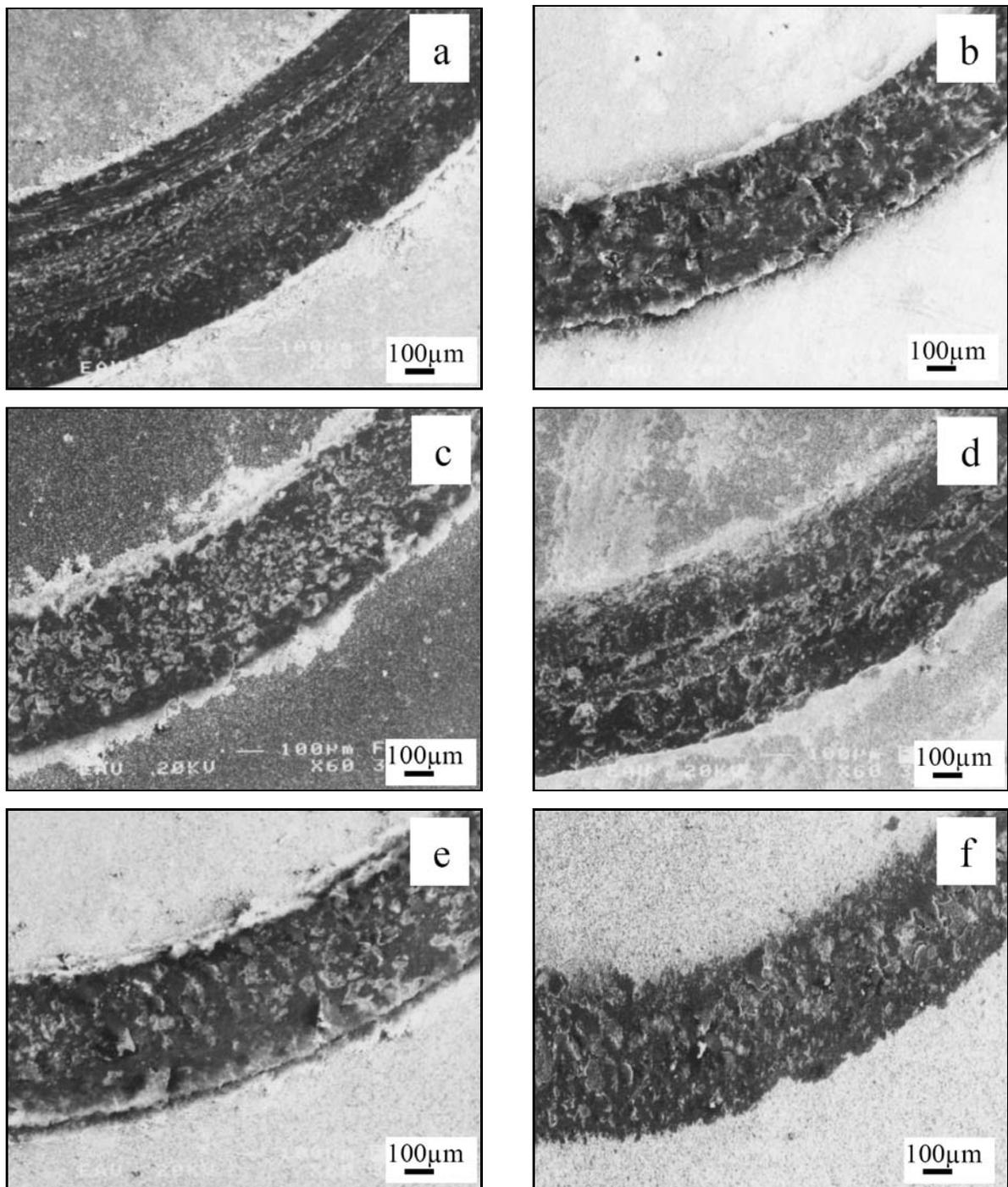


Fig. 7. SEM micrograph of wear tracks: a) ferritic NC, b) FNC + oxidizing (O_2), c) FNC + oxidizing (O_2/H_2), d) austenitic NC, e) ANC + oxidizing (O_2), f) ANC + oxidizing (O_2/H_2).

reduction in the friction coefficient and a more stable condition were observed. While the friction coefficient exhibited an unstable behaviour from the beginning to 550 th in untreated samples, stable conditions were attained later. Figure 4 shows the effect of ferritic nitrocarburizing and post-oxidation treatments on the friction coefficient. The friction coefficient of the ferritic nitrocarburized samples previously was reduced

by starting from high values, but reached a stable state in a short time. The lowest friction coefficient for the ferritic conditions was obtained with the oxidation carried out under a gas atmosphere with hydrogen. A significant difference is not seen in the friction characteristics of the treated samples while lower and more stable friction coefficient is observed in the nitrocarburized and post-oxidized

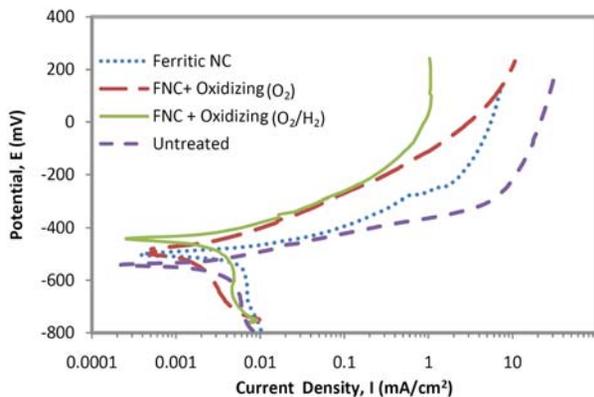


Fig. 8. Potentiodynamic polarization curves for ferritic nitrocarburized and post-oxidized AISI 4140 steel.

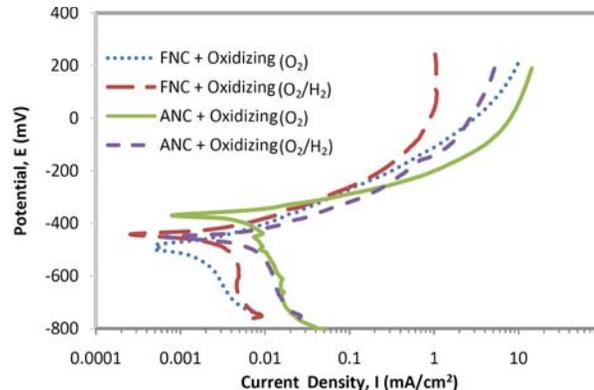


Fig. 10. Potentiodynamic polarization curves for nitrocarburized and post-oxidized AISI 4140 steel.

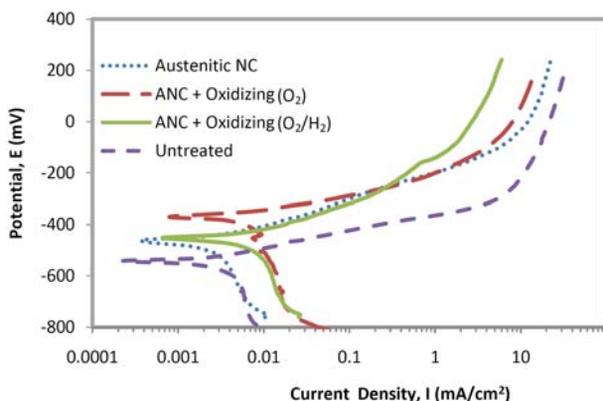


Fig. 9. Potentiodynamic polarization curves for austenitic nitrocarburized and post-oxidized AISI 4140 steel.

samples under austenitic conditions when compared with untreated samples (Fig. 5). The untreated and oxidized samples are compared in Fig. 6. While low and stable friction is seen for oxidized samples, a great change in the coefficient is not observed with oxidation conditions. The lowest friction was obtained with the oxidation carried out under the atmosphere with hydrogen, a very small difference though.

Figure 7 shows SEM photos of wear tracks of the samples tested with pin-on-disc wear. It is observed that the width of the wear track of all oxidized samples is narrower than that of only nitrocarburized samples. This demonstrates that the wear rate of the nitrocarburized specimen is higher.

Figures 8, 9 and 10 show potentiodynamic polarization curves of the untreated, nitrocarburized and post-oxidized AISI 4140 steel in 3.5 % NaCl. In Fig. 8, the effect of post-oxidation on corrosion behaviour after nitrocarburizing and ferritic nitrocarburizing (570°C) is shown. As shown in Fig. 8, the corrosion properties of both the nitrocarburized and

post-oxidized samples were improved. Corrosion potential increased and anodic current density decreased after the treatments. The highest decrease at the anodic current densities was obtained with the oxidation achieved under a gas atmosphere with hydrogen after nitrocarburizing. Corrosion potentials after the ferritic nitrocarburizing and post oxidizing treatments were more positive than that of the untreated steels. The highest increase at the corrosion potential was obtained with the oxidation carried out under a gas atmosphere with hydrogen after nitrocarburizing again. The corrosion potential rose from about -540 mV (untreated) to -420 mV with this treatment. Figure 8 also demonstrates that the corrosion current densities of the treatments were close to each other.

Figure 9 shows the effect of post-oxidation on corrosion behaviour after nitrocarburizing and austenitic nitrocarburizing (700°C). Positive effect of the post-oxidation on corrosion resistance was observed, which is similar to ferritic conditions. It was observed in Fig. 9 that the corrosion resistance increased as a result of austenitic nitrocarburizing and nitrocarburizing + post-oxidizing compared with untreated sample. After all the treatments, anodic current densities decreased compared to the untreated sample. Also, the corrosion potential shifted to more positive values after the treatments. A major change was not observed in the corrosion current densities.

In Fig. 10, polarization curves obtained after ferritic and austenitic nitrocarburizing + post-oxidizing are illustrated to demonstrate the effect of the post-oxidation on corrosion behaviour carried out in a variety of gas atmospheres. As seen from polarization curves, higher corrosion potential and relatively lower anodic current density in a post-oxidation process where hydrogen is used in plasma atmosphere, when compared to the post-oxidation treatments in which only oxygen is used in plasma atmosphere. For example, at a corrosion potential of 0 mV, the highest current density was observed at about 10 mA cm^{-2}

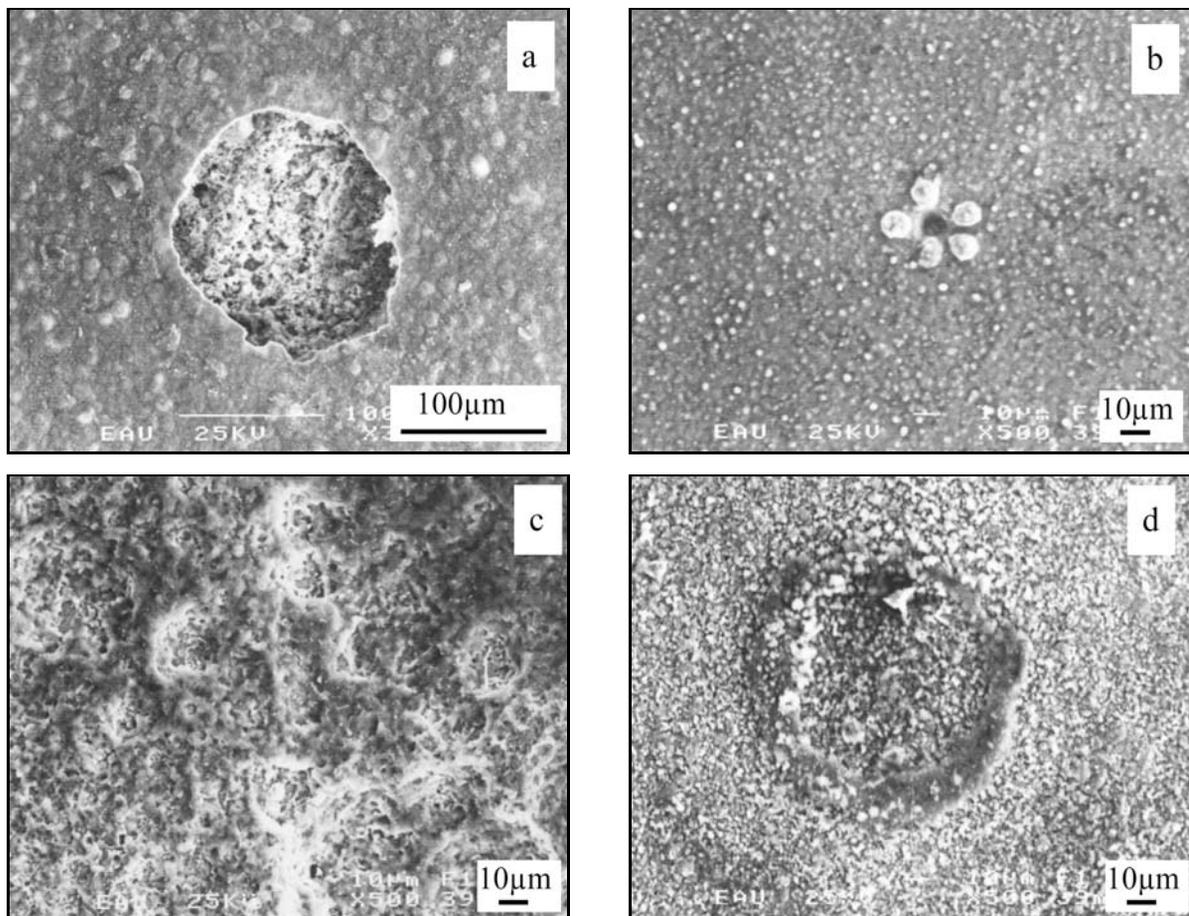


Fig. 11. SEM micrographs of the surface of the specimens after polarization test: a) ferritic NC + oxidation in pure oxygen, b) ferritic NC + oxidation in oxygen/hydrogen, c) austenitic NC + oxidation in pure oxygen, d) austenitic NC + oxidation in oxygen/hydrogen.

for post-oxidation carried out under pure oxygen atmosphere after austenitic nitrocarburizing. However, the lowest current density was obtained at 1 mA cm^{-2} for the post-oxidation under the atmosphere with hydrogen after ferritic nitrocarburizing.

It can be seen from Figs. 8, 9 and 10, that the corrosion behaviour improved for both ferritic plasma nitrocarburized and austenitic plasma nitrocarburized samples compared to the untreated samples. It was also observed that the improvement in the corrosion resistance increased more with the post-oxidation of the nitrocarburized samples. The corrosion resistance increased more due to thin and dense oxide layers consisting of hematite (Fe_2O_3) and magnetite (Fe_3O_4) phases formed on the compound layer after post-oxidation treatments. A modification in nitrocarburizing was realized with the effect of compound layer composed of $\varepsilon\text{-Fe}_{2-3}(\text{N}, \text{C})$ and/or $\gamma'\text{-Fe}_4(\text{N}, \text{C})$ phases surrounding the sample surface. This appears to be due to the formation of a thin oxide film at the outermost surface, which covers and seals microvoids and microcracks on top of the nitrocarburized layer [10,

13]. As mentioned before, magnetite has more corrosion resistance than hematite because it is denser and more compact with better adhesion to compound layer [8, 9].

SEM micrographs of the surface of the specimens after polarization test are shown in Fig. 11.

4. Conclusion

The following main conclusions can be derived from the above results:

- Oxide layer includes hematite (Fe_2O_3) and magnetite (Fe_3O_4) phases while the compound layer formed after both ferritic and austenitic nitrocarburizing includes $\varepsilon\text{-Fe}_{2-3}(\text{N}, \text{C})$ and $\gamma'\text{-Fe}_4(\text{N}, \text{C})$ phases.

- Post-oxidation improved more wear properties while wear resistance of the ferritic and austenitic nitrocarburized samples increased. While less wear occurred for austenitic conditions in nitrocarburizing, it was determined that better wear properties were ob-

tained with post-oxidation after ferritic nitrocarburizing and the lowest wear rate was obtained with the oxidation carried out under a plasma atmosphere with hydrogen after ferritic nitrocarburizing.

– When compared with the untreated samples, it was seen that the values of the friction coefficient were reduced after each treatment and were more stable. The lowest friction coefficient of about 0.25 was obtained after oxidation carried out under a gas atmosphere with hydrogen after austenitic nitrocarburizing.

– The corrosion resistance increased after each treatment when compared with the untreated samples. The best corrosion properties were obtained with the oxidation under plasma atmosphere with hydrogen after ferritic nitrocarburizing.

To conclude, the oxidation treatment after nitrocarburizing has contributions to tribological and corrosion properties. The positive effect of the post-oxidation is more than that of ferritic nitrocarburizing compared to the treatments carried out under austenitic conditions.

Acknowledgements

This research has been supported by Ataturk University, Research Funded by grant no. 2005/13. The authors wish to thank A. Fatih Yetim and Prof. Dr. İhsan Efeoğlu for their valuable assistance in tribological tests.

References

- [1] KARAKAN, M.—YETIM, A. F.—ÇELİK, A.: *Kovove Mater.*, 44, 2006, p. 139.
- [2] SOMERS, M. A. J.: *Heat Treat. Met.*, 4, 2000, p. 92.
- [3] ÇELİK, A.—ARSLAN, Y.—YETIM, A. F.—EFEOĞLU, I.: *Kovove Mater.*, 45, 2007, p. 35.
- [4] ASHRAFIZADEH, F.: *Surf. Coat. Tech.*, 173–174, 2003, p. 1196.
- [5] LI, C. X.—SUN, Y.—BELL, T.: *Mat. Sci. Eng. A*, 292, 2000, p. 18.
- [6] KARAKAN, M.—YETIM, A. F.—ÇELİK, A.—ALSARAN, A.: *Kovove Mater.*, 46, 2008, p. 173.
- [7] BELL, T.—SUN, Y.—SUHADI, A.: *Vacuum*, 59, 2000, p. 14.
- [8] ALSARAN, A.—ALTUN, H.—KARAKAN, M.—ÇELİK, A.: *Surf. Coat. Tech.*, 176, 2004, p. 344.
- [9] ESFAHANI, A.—SOHI, M. H.—RASSIZADEHGHANI, J.—MAHBOUBI, F.: *Vacuum*, 82, 2008, p. 346.
- [10] JEON, E. K.—PARK, I. M.—LEE, I.: *Mat. Sci. Eng. A*, 449–451, 2007, p. 868.
- [11] LEE, I.: *Rare Metals*, 25, 2006, p. 614.
- [12] LEE, K. H.—NAM, K. S.—SHIN, P. W.—LEE, D. Y.—SONG, Y. S.: *Mat. Lett.*, 57, 2003, p. 2060.
- [13] LEE, I.: *Surf. Coat. Tech.*, 188–189, 2004, p. 669.
- [14] OKADO, J.—OKADA, K.—ISHIYAMA, A.—SETSUHARA, Y.—TAKENEKA, K.: *Surf. Coat. Tech.*, 202, 2008, p. 5595.
- [15] SUN, Y.: *Tribology Int.*, 40, 2007, p. 208.
- [16] ZLATANOVIĆ, M.—POPOVIĆ, N.—BOGDANOV, Ž.—ZLATANOVIĆ, S.: *Surf. Coat. Tech.*, 177–178, 2003, p. 277.
- [17] BELL, T.—KINALI, M.—MUNSTERMANN, G.: *Heat Treat. Met.*, 2, 1987, p. 47.
- [18] LI, S.—MANORY, R. R.—HENSLER, J. H.: *Surf. Coat. Tech.*, 71, 1995, p. 112.
- [19] ÇELİK, A.—KARAKAN, M.—ALSARAN, A.—EFEOĞLU, I.: *Surf. Coat. Tech.*, 200, 2005, p. 1926.
- [20] KARAKAN, M.: Investigation of Structural, Mechanical and Tribological Properties of Plasma Nitrocarburized AISI 4140 and 1020 Steels. [Ph.D. Thesis]. Erzurum/Turkey, Ataturk University (in Turkish) 2004.