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Duplex Surface Treatments of Plasma Nitrocarburizing and Plasma Oxidation of SKD 11 Steel

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Abstract

Plasma nitrocarburizing and plasma oxidizing treatments were performed to improve the wear and corrosion resistance of SKD 11 steel. Plasma nitrocarburizing was conducted for 12 h at 520°C in the nitrogen, hydrogen and methane atmosphere to produce the ε-$Fe_{2\text{-}3}(N,C)$ phase. It was found that the compound layer produced by plasma nitrocarburising was predominantly composed of ε-phase, with a small proportion of γ'-$Fe_4(N,C)$ phase. The thickness of the compound layer was about 5 μm and the diffusion layer was about 150 μm in thickness, respectively. Plasma post oxidation was performed on the nitrocarburized samples with various oxygen/hydrogen ratio at constant temperature of 500°C for 1 hour. The very thin magnetite (Fe_3O_4) layer 1-2 μm in thickness on top of the compound layer was obtained by plasma post oxidation. It was confirmed that the corrosion characteristics of the nitrocarburized compound layer could be further improved by the application of the superficial magnetite layer.

Keywords: Plasma nitrocarburizing, Post oxidation, ε-$Fe_{2\text{-}3}(N,C)$, γ'-$Fe_4(N,C)$, Fe_3O_4

1. Introduction

Recently, plasma ion nitriding has received a great attention due to its reduced distortion and environment-friendly process. The plasma ion nitriding is a thermo-chemical process to improve the surface properties, such as wear resistance, corrosion resistance, and fatigue strength, of various engineering steels. Plasma nitrocarburizing is a process in which a small amount of carbon-containing gases such as CH_4 and C_3H_8 is added to the gas mixture of N_2 and H_2 employed for the glow discharge plasma nitriding method[1]. It introduces nitrogen and carbon atoms together into the surface of ferrous materials to produce an outer ε-$Fe_{2\text{-}3}(N,C)$ compound layer and an inner diffusion layer. However, it has been reported that it is rather difficult to produce a single ε-$Fe_{2\text{-}3}(N,C)$ phase compound layer on plain carbon steel. Instead, by plasma nitrocarburizing process, a compound layer with mixed ε-$Fe_{2\text{-}3}(N,C)$ and γ'-$Fe_4(N,C)$ phases, which has a harmful effect on tribological properties, is obtained. It is possible to generate a duplex hardened layer by producing an oxide film of Fe_3O_4 on top of the compound layer in the glow discharge of a plasma-containing oxygen after plasma nitrocarburizing. It is reported that under severe conditions, the duplex layer reveals better surface properties such as wear resistance, adhesion resistance and self-lubrication. It is also known that the grown oxide film leads to a significant improvement of the corrosion resistance of iron-based materials[2-4]. Therefore, by proper control of the plasma oxidation temperature and time, it was possible to produce an adherent Fe_3O_4 film of 1-2 μm in thickness on top of the plasma nitro-carburized ε-phase compound layer. The present paper presents the surface characteristics of the hardened layer produced on SKD 11 steel by the plasma nitrocarburizing and then post oxidation processes.

2. Experimental Procedure

The material used for this investigation is SKD 11

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Table 1. Chemical composition of SKD 11 Steel

Fe	Fe	C	Cr	Mo	Si	Mn	V
Bal	Bal	1.50	12.0	1.00	0.25	0.45	0.35

steel which is a commercially used alloy steel for cold forging die for automotive parts. The chemical composition of SKD 11steel is tabulated in Table 1. The cylindrical samples (ϕ 22 mm × h 8 mm) were heated at 1020°C for 2 hours, oil quenched, tempered at 480°C for 2 hours, and air cooled. The surfaces of the cylindrical samples to be exposed to the plasma were polished and then cleaned. The phase of the surface was identified as α-Fe (BCC structure). The vacuum chamber was pumped down to 6.6 Pa (50 mTorr) and then Ar and H_2 ion sputtering was performed at 300°C for 40 minutes for further surface cleaning (voltage: 380 V, gas composition: Ar/H_2= 80/20%, pulse: on/off time = 1500 μs/15 μs, time: 40 min). After cleaning, the plasma nitrocarburizing process was immediately carried out with a pulsed d.c. potential at 520°C for 12 hours in the glow discharge of a gas mixture of N_2, H_2, and CH_4 (voltage: 500 V, gas pressure: 399 Pa (3 Torr), pulse: on/off time = 135 μs/15 μs). After treatment, the vacuum chamber was evacuated again and the samples were cooled in the chamber to oxidation temperature. Plasma oxidation process was conducted in the glow discharge of a gas mixture of O_2 and H_2 (pressure: 399 Pa (3 Torr)) at 500°C for 1 hour. After the plasma oxidation, the vacuum chamber was pumped down to 6.6 Pa (50 mTorr) and the samples were cooled in the vacuum chamber to room temperature. The microstructures of oxide and nitrocarburizd layers on the surface were observed by optical microscopy and scanning electron microscopy (SEM). A Rigaku D/Max-200 X-ray diffractometer was used to analyse the phases formed on the plasma nitrocarburized/post oxidized surfaces of the specimens. Microhardness measurements were carried out with a Micro Vickers microhardness tester at a constant load of 1.96 N (200 g) and a loading time of 15 second. At each depth, 10 measurements were taken and then the mean value was determined by averaging 8 measurements, excluding the highest and the lowest values. Potentiostat polarization technique was employed to estimate the corrosion characteristics of the oxynitrocarburized layer in 3% NaCl solution. A Saturated Calomel Electrode was selected for the reference electrode and carbon rod was used for the counter electrode.

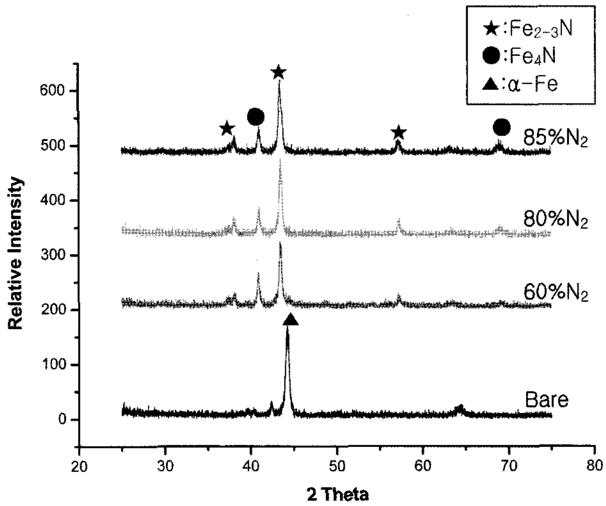

Fig. 1. XRD patterns of compound layers of SKD 11 steel treated with various N_2 gas compositions (fixed CH_4: 3%).

3. Results and Discussion

3.1 Plasma Nitrocarburizing of SKD 11 Steel

Fig. 1 reveals X-ray diffraction spectra of compound layer on SKD 11 steel obtained from plasma nitrocarburization process at 520°C for 12 hours, at a pressure of 3 Torr, using various N_2 gas composition (60, 80, 85%) with fixed CH_4 gas composition (3%). It can be seen that with increasing nitrogen content from 60% to 85%, the relative amount of ε phase in the compound layer increases and that of γ' phase decreases. However, further increase of nitrogen content of 80% to 85% has no influence on the relative ratio of ε phase and γ' phase. The thickness of the compound layer is also observed to increase with nitrogen content in a gas mixture. This appears to be due to enough active nitrogen ions in a gas mixture with a high nitrogen content. It has been recognized that in comparision to γ' phase, ε phase has much wider solubility range of nitrogen, which enables to produce a steeper concentration gradient. This will facilitate faster growth of ε phase. Thus the thickness of the compound layer increases rapidly as the nitrogen composition in a gas mixture increases.

Fig. 2 shows the typical compound layer morphology produced on SKD 11 steel by plasma nitrocarburizing in $N_2/H_2/CH_4$ (80/17/3) atmosphere at 520°C for 12 hours. A nitrocarburized compound layer about 6 μm in thickness, composed predominantly of ε-Fe_{2-3}(N,C) and a small amount of γ'-Fe_4(N,C) phase, was produced by plasma nitrocarburizing treatment. GDS (Glow Discharge Spectroscopy) data show that the compound layer formed contains about 7 wt% N and 2 wt% C.

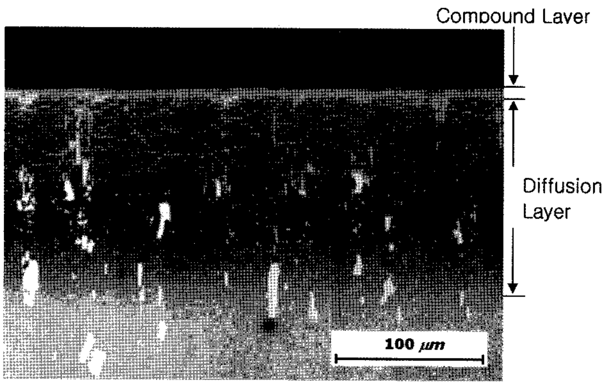

Fig. 2. Optical micrograph showing compound and diffusion layers produced on on SKD 11 steel by plasma nitrocarburizing in $N_2/H_2/CH_4$ (80/17/3) atmosphere at 520°C for 12 hours.

According to the Fe-N-C ternary phase diagram at 570°C, Such a nitrocarburized compound layer corresponds to a single ε field. In addition, it has been known that the γ'-phase has been produced by decomposition of the ε-phase layer during slow furnace cooling[1]. Micropores are observed, in the compound layer. Underneath the compound layer, a nitrogen diffusion zone of 150 μm in thickness was formed. The diffusion layer contained iron and alloy element nitride precipitates dispersed in the nitrogen diffused interstitial solid solution of iron.

3.2 Plasma Post Oxidation of SKD 11 Steel

Fig. 3 exhibits X-ray diffraction spectra of specimens with various oxygen/hydrogen ratio at oxidation temperature of 500°C for 1 hour after plasma nitrocarburizing in $N_2/H_2/CH_4$ (80/17/3) atmosphere at 520°C for 12 hours. It can be seen that a single phase magnetite (Fe_3O_4) can be produced in an atmosphere containing O_2/H_2 composition more than 10%. However, for the O_2/H_2 composition of 5%, there is a little oxide formation due to insufficient amount of active oxygeon ions in a gas mixture with a low oxygen content. Whilst, it has been recognized that for the O_2/H_2 composition more than 20%, cementite θ-Fe_3C can be produced in the compound layer. The formation of θ-Fe_3C is also associated with dissociation of ε-$Fe_{2\text{-}3}$(N,C) phase during O_2/H_2 plasma sputtering. Nitrogen, carbon, and iron atoms are emitted during the sputtering process. Beneath the oxide layer, the Fe_3C phase was produced by recombining iron atoms and sputtered carbon atoms which diffuse through the oxide layer[5]. Therefore, the atmosphere with O_2/H_2 composition of about 15% is detemined to the optimum condition for the production of a single phase magnetite (Fe_3O_4).

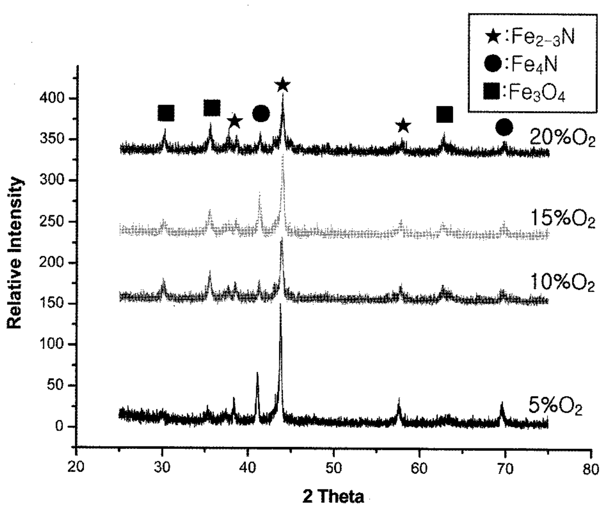

Fig. 3. XRD patterns of oxide layer produced on SKD 11 steel treated with various oxygen hydrogen ratios at 500°C for 1 hour after plasma nitrocarburizing in $N_2/H_2/CH_4$ (80/17/3) atmosphere at 520°C for 12 hours.

Fig. 4 is the cross-section showing typical morphology of the oxide film and compound layer produced on SKD 11 steel by plasma nitrocarburizing at 520°C for 12 hours and then plasma oxidation at 500°C for 1 hour. An oxide film about 1-2 μm in thickness on top of the compound layer is produced. It can be seen that the compound layer and micropores are covered with the superficial oxide film. It has been recognized that the corrosion resistance of the nitrocarburized layer can be further improved by oxidation treatment.

This can be attributed to the formation of the oxide film. In addition, it has been reported that the wear resistance can be further improved by oxidation treatment of the nitrocarburized layer. This can be ascribed to the lower friction coefficient of the Fe_3O_4,

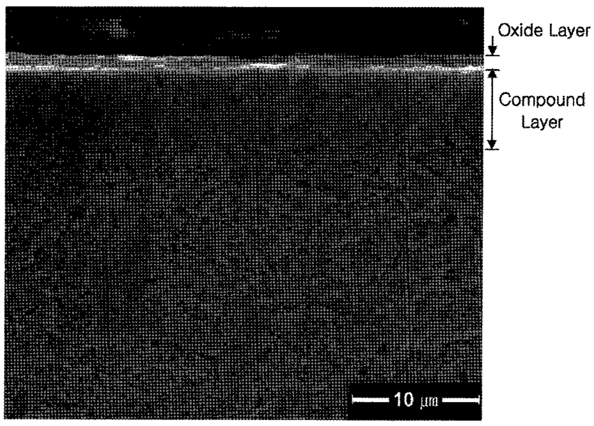

Fig. 4. Scannig electron micrograph of the cross-section of SKD 11 steel, showing the morphology of the compound layer and oxide film after the plasma nitrocarburizing and then post oxidation processes.

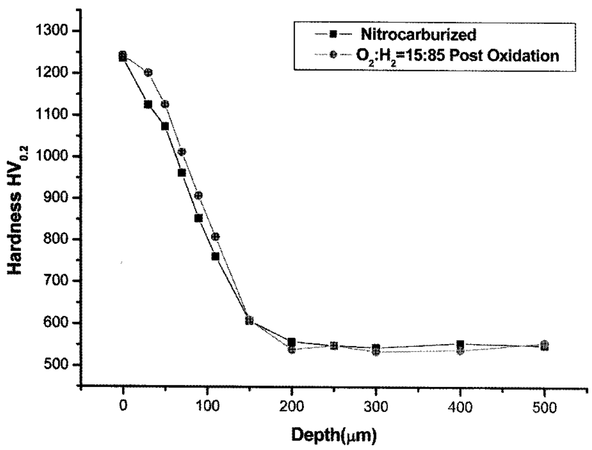

Fig. 5. Microhardness profiles of the surface hardened layer of SKD 11 steel.

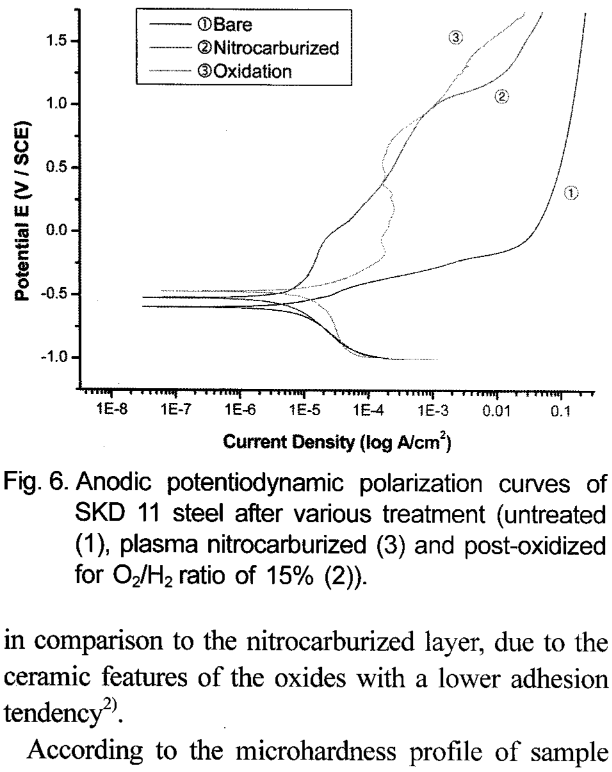

Fig. 6. Anodic potentiodynamic polarization curves of SKD 11 steel after various treatment (untreated (1), plasma nitrocarburized (3) and post-oxidized for O_2/H_2 ratio of 15% (2)).

in comparison to the nitrocarburized layer, due to the ceramic features of the oxides with a lower adhesion tendency[2].

According to the microhardness profile of sample (Fig. 5) by plasma nitrocarburizing at 520°C for 12 hours and then plasma oxidation at 500°C for 1 hour, the surface hardness value reaches about $HV_{0.2}$ 1250 (12.5 GPa) and the case depth is about 150 μm. It has been anticipated that post oxidation treatment causes a reduction in surface hardness value, due to the relatively low hardness of iron oxide. However, there is no reduction in surface hardness in comparison to the sample treated with nitrocarburizing alone. This is attributed to the relatively low thickness of the oxide layer on top of the nitrocarburized compound layer.

Fig. 6 reveals the effect of nitrocarburizing and post oxidation treatment on the corrosion behavior of the SKD 11 steel. It can be seen that in 3% NaCl solution, plasma nitrocarburizing process contributes a significant improvement of the corrosion resistance of SKD 11 steel. In addition, the corrosion characteristics of nitrocarburized steel components can be further improved by oxidation treatments. The post-oxidized sample under 15% oxygen-containing atmosphere shows higher corrosion potential and lower corrosion current density as compared with those treated nitrocarburizing. This can be attributed to the formation of a stable oxide Fe_3O_4 layer which covers completely the whole nitrocarburized compound layer after the oxidation treatment. It is clear that plasma nitrocarburizing and post-oxidation processes improves the corrosion resistance of steel components. 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.

4. Conclusions

Plasma nitrocarburizing process produces a compound layer composed predominantly of ε phase on the surface of SKD 11 steel in a gas mixture of N_2:H_2:CH_4 = 80:17:3. The thickness of the nitrocarburized compound layer was identified to be about 6 μm and diffusion layer was determined to be about 15 μm, respectively. Both the thickness of the compound layer and the relative amount of ε phase in the compound layer increase with nitrogen content. Plasma Post Oxidation resulted in the formation of a single phase magnetite (Fe_3O_4) layer of 1~2 μm in thickness on top of nitrocarburized layer. Anodic polarization test revealed that plasma nitrocarburizing and post oxidation processes contributed a significant improvement of corrosion resistance of SKD 11 steel.

Acknowledgements

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References

1. T. Bell, Y. Sun, A. Suhadi, Vacuum, 59 (2000) 14.
2. S. Hoppe, Surf. Coat. Technol., 98 (1998) 1199.
3. F. Borgioli, E. Galvanetteo, A. Fossati, T. Bacci, Surf. Coat. Technol., 162 (2002) 61.
4. R. H. Jutte, B. J. Kooi, M. A. J. Somers, E.J. Mittemeijer, Oxid. Metals, 48 (1997) 87.
5. Insup Lee, Surf. Coat. Technol., 188-198 (2004) 669.