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PLASMA-SULFNITRIDING USING HOLLOW CATHODE DISCHARGE

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ABSTRACT

In order to plasma-sulfnitride by combining ion-nitriding of a steel and sputtering of MoS₂, chromium-molybdenum steel was plasma-sulfnitrided using hollow cathode discharge with parallel electrodes which are a main of the steel and a subsidiary cathode of MoS₂. The treatment was carried out at 823K for 10.8ks under 665Pa in a 30% N₂-70% H₂ gas atmosphere. Plasma-sulfnitriding layers formed of the steel were characterized with EDX, XRD, micrographic structure observation and hardness measurement.

A compound layer of 8-15 μ m and nitrogen diffusion layer of about 400 μ m were formed on the surface of plasma-sulfnitrided steel. The compound layer consisted of FeS containing Mo and iron nitrides. The nitrides of ϵ -Fe₂₋₃N and γ '-Fe₄N formed under the FeS. The thickness of compound layer and surface hardness were different with the gaps between main and subsidiary cathodes even in the same sulfnitriding temperature. The surface hardnesses after plasma-sulfnitriding were distributed from 640 to 830Hv. The surface hardness was higher in the plasma-sulfnitriding than the usual sulfnitriding in molten salt. This may be due to Mo in sulfnitriding layer.

INTRODUCTION

Sulfnitriding is a surface hardening treatment to give wear, fatigue and corrosion resistance to the steel and also effective way to provide lubrication to the surface of hardened steel, but the usual gas and liquid sulfnitriding have the disadvantage that poisonous substances such as hydrogen sulfide gas and sodium cyanide salt are used^[1-4].

Ion-nitriding is pollutionless and energy-saving surface hardening treatment^[5-7]. The treatment uses direct current glow discharge in reduced pressure including nitrogen and hydrogen. Negative and positive potential are

applied to a steel and chamber wall as a cathode and anode respectively. When the electric potential applied to them, glow discharge generate around the steel and the steel is heated by bombardment of the positive gas ions and nitrogen diffuses into the steel.

It is known that a electric discharge with strong ionization of gas and radiation of light occurs in the inner wall of a metallic cylinder to which an electric potential is applied under gas atmosphere of about 10³ Pa. This phenomenon is called as hollow cathode discharge^[8, 9]. Gas ion concentration in hollow cathode discharge reaches several times more than normal glow discharge. The hollow cath-

ode type discharge can also generate by applying a negative electric potential between two metallic plates under suitable gas atmosphere. The metallic plates can be heated to high temperature by hollow cathode discharge, and easily sputtered by bombardment of the increased positive gas ions and heating of the plates^[10]. The sputtered atoms of the plates move to the opposite metallic plate surfaces through the plasma space^[11]. In this study, A plate of low carbon steel is placed on a sample holder of a cathode. A plate of MoS₂, which is a good lubricant, is set parallel to the steel with a small gap to generate hollow cathode discharge between the two plates and to accelerate sputtering of MoS₂. Thus, the steel can be plasma-sulfnitrided by combination of ion-nitriding and sputtering of MoS₂ using hollow cathode discharge. The plasma-sulfnitrided steel was investigated metallographically^[12].

EXPERIMENTAL PROCEDURE

The sample for sulfnitriding was made of SCM435. The chemical compositions of the SCM435 are shown in Table 1. The steel was quenched into water after heating at 1123K for 3.6ks. The quenched steel was tempered at 873K for 3.6ks. The steel was cut to 12mm × 10mm × 5mm. Before sulfnitriding, the steel was polished with emery paper of No. 1600 and diamond-paste of 0.25 μ m dia. and then, ultrasonically cleaned in acetone.

A plasma-sulfnitriding apparatus is shown

Table 1. Chemical compositions of SCM435.
(wt%)

C	Si	Mn	P	S	Cr	Mo	Fe
0.33	0.23	0.72	0.030	0.030	1.07	0.15	Bal.

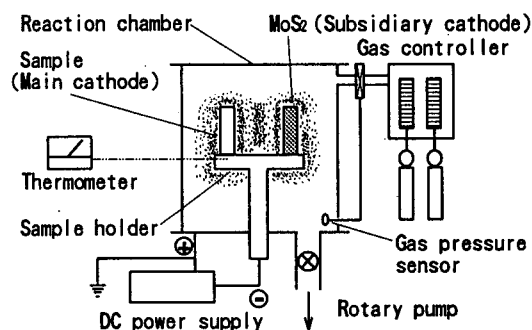


Fig. 1 Schematic drawing of plasma-sulfnitriding apparatus.

schematically in Fig. 1. The apparatus has a cathode and anode which has a sample holder and reaction chamber wall respectively. A sulfnitriding sample of a steel plate was put on the sample holder of a cathode. MoS₂ is 12 mm × 10 mm × 5 mm. After setting the sample and MoS₂ plate, the reaction chamber was evacuated under 1.33 × 10⁻¹ Pa. First, the surfaces of the sample and MoS₂ plate were sputtered to clean for about 20 min in a dc glow discharge under the reduced H₂ gas. After the sample was cleaned, the reaction chamber was evacuated under 1.33 Pa. The sample was heated to setting temperature by glow discharge and plasma-sulfnitrided at 823K for 10.8 ks in an atmosphere of 30% N₂-70% H₂ mixing gas at 665 Pa. After plasma-sulfnitriding, the sample was cooled down in evacuating condition. The gap between the sample and MoS₂ plate was changed to 3~10 mm. The experimental conditions for plasma-sulfnitriding are shown in Table 2. Discharge voltage was controlled at about 400 V. The temperature of the sample was measured with a chromel-alumel thermocouple embedded in the sample holder.

Chemical components of compound layers

of the plasma-sulfnitrided steel were analyzed with an energy-dispersive X-ray (EDX) spectroscopy. Precipitates were identified by X-ray diffraction (XRD) using $\text{Co-K}\alpha$ source. The tube voltage was 30kV. The surface morphology and cross-sectional structure were observed by a scanning electron microscope (SEM) and an optical microscope (OM). All the samples were etched for 3sec with 3% nital. Hardness was measured by loading 100 g for 30s with a micro-Vickers hardness tester. Mean hardness values were obtained from ten points measure.

Tabel. 2 Experimental conditions.

Gas pressure	665Pa
Treatment time	10.8ks
Gap between sample and MoS_2	3, 6, 10mm
Ratio of N_2/H_2	3.7
Sulfnitriding temperature	823K
Discharge current	0.25A

RESULTS AND DISCUSSION

Chemical components of the surface layer

Fig. 2 shows the EDX spectra obtained from the steel which was plasma-sulfnitrided

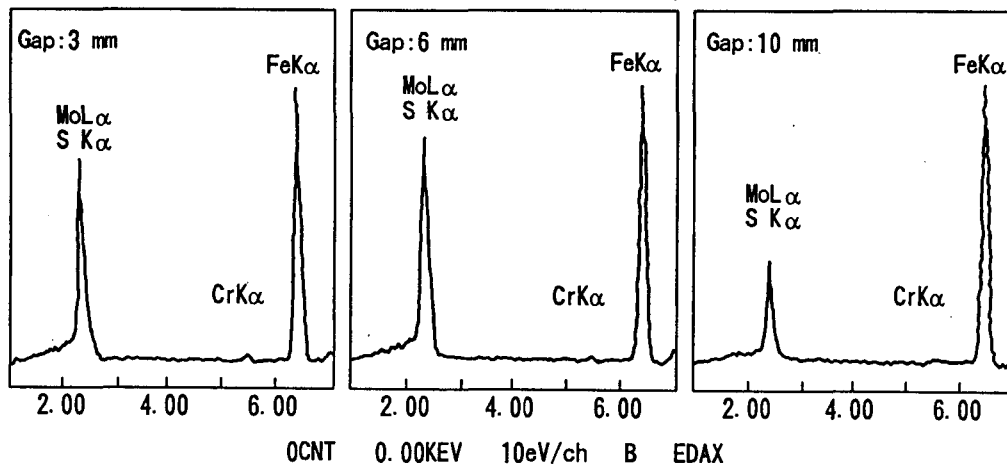


Fig. 2 EDX spectra of the plasma-sulfnitrided SCM435.

in the gaps of 3~10mm. When the gaps between the steel and MoS_2 are 3, 6 and 10mm, Mo and S peaks were detected from all plasma-sulfnitrided steel surfaces. This means that Mo and S atoms sputtered and/or thermally decomposed from MoS_2 of the subsidiary cathode reach on the surface of the steel of the main cathode traveling through plasma space between them and then deposit on the steel surface. The heights of Fe peak in the EDX spectra are similar, but the peaks of Mo and S in the gap of 6mm are a little higher than those in 3mm and fairly higher than in 10mm.

Precipitates

Fig. 3 shows X-ray diffraction patterns of the steel plasma-sulfnitrided at 823K for 10.8ks in a 30% N_2 -70% H_2 mixing gas at 665Pa. As the peaks of FeS and $\epsilon\text{-Fe}_{2-3}\text{N}$ were detected at the same diffraction angle of 51.5 degree from the surfaces of the plasma-sulfnitrided steel, the separation of FeS and $\epsilon\text{-Fe}_{2-3}\text{N}$ peaks is difficult, but it is considered that FeS is formed in the sulfnitrided surface layer from the above EDX results that intensities of Mo and S are quite strong. In addition, the diffusion rates of Mo and S

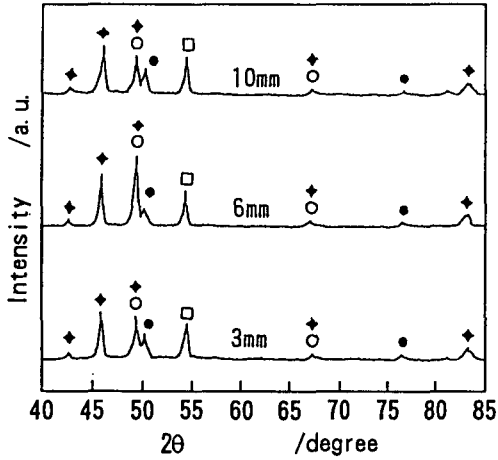


Fig. 3 X-ray diffraction patterns of the plasma-sulfnitrided SCM435. (\blacklozenge : ϵ -Fe₂₋₃N, \square : γ -Fe₄N, \circ : FeS, \bullet : α -Fe)

atoms in α -Fe are much smaller than that of nitrogen, so Mo and S are very difficult to be diffused into the steel and form thin FeS layer on the steel surface. From the results, it can be seen that Mo and S sputtered and/or evaporated from MoS₂ travel to the steel at opposite side and deposit on the steel surface even in the high pressure of 665Pa for sputtering and then make the thin FeS layer on the steel surface. The peaks of FeS and ϵ -Fe₂₋₃N in the gap of 6mm were a little higher than in 3 and 10mm.

Surface morphology and cross-sectional structures

Fig. 4 shows SEM images of MoS₂ surfaces before plasma-sulfnitriding treatment and exposed to direct current plasma during plasma-sulfnitriding. Surface of the MoS₂ is rough and has sharp edge. The surface of MoS₂ exposed in direct current plasma for 10.8ks in the gap of 6mm was covered with fine grain-like precipitates of about 0.5 μ m size, because the Mo and S atoms sputtered and/or evaporated from MoS₂ are re-deposited on the same MoS₂ surface after repeating corrosion with gas atoms.

Fig. 5 shows cross-sectional micrographs of the plasma-sulfnitrided steel. The surfaces of the steel plasma-sulfnitrided in the gap of 3~10mm were covered with white layers of about 8~15 μ m thick. The top part of the white layers was made of FeS containing Mo. It is known from the results of the X-ray diffraction analysis that the iron nitrides of ϵ -Fe₂₋₃N and γ -Fe₄N are formed under the FeS layer. The thickness of compound layers is different with the gaps between the steel and MoS₂. In the gap of 6mm, the compound

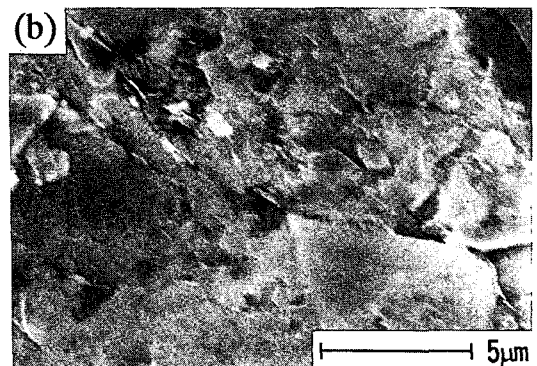
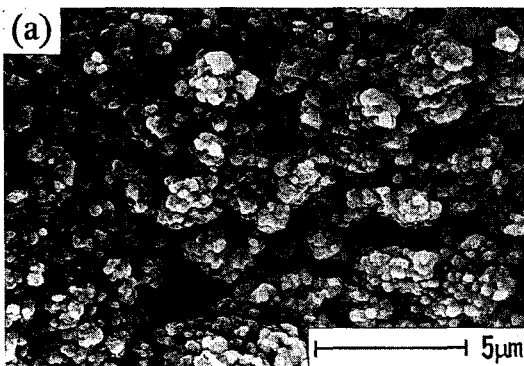


Fig. 4 SEM images of MoS₂ surfaces. (a) Before plasma-sulfnitrided, and (b) exposed in direct current plasma for 10.8ks in an atmosphere of 30% N₂-70% H₂ mixing gas at 665Pa.

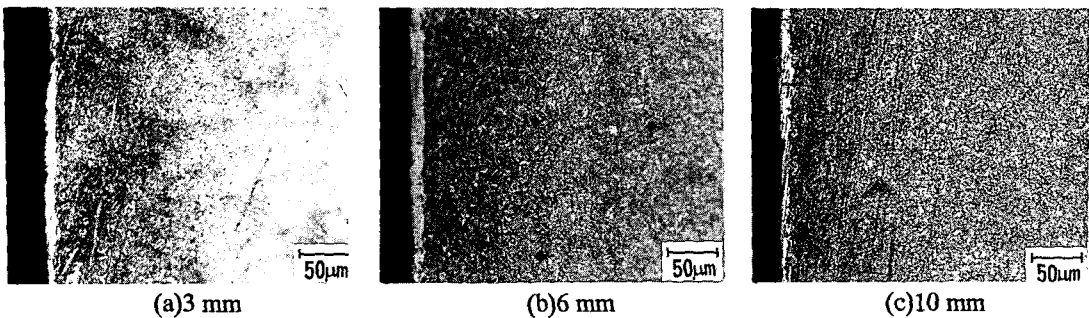


Fig. 5 Cross-sectional micrographs of SCM435 plasma-sulfnitrided in different gaps between steel and MoS_2 .

layer formed on the steel surface was thicker and flatter than in the gap of 3 and 10mm as seen in Fig. 5.

Hardness

Fig. 6 shows hardness distributions of the steel plasma-sulfnitrided in different gaps between the steel and MoS_2 . The hardness value, which was measured from surface, was different with the gaps. As shown in Fig. 6, the hardness value in the matrix of the steel was similar in the steel plasma-sulfnitrided in different gaps but the surface hardness value was distributed from 640 to 830Hv. The surface was harder when the gap

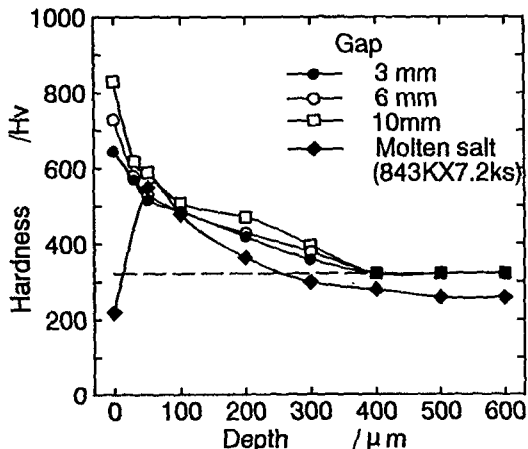


Fig. 6 Hardness distributions of the plasma-sulfnitrided SCM435.

between steel and MoS_2 plates was larger.

The surface hardness of the steel plasma-sulfnitrided in the gap of 10mm may be measured as high value, as the thinnest and soft FeS layer is formed over hard nitrides. The layer of approximately $400\mu\text{m}$ thick from surface was nitrogen diffusion layer. The hardness of the diffusion layer was approximately 600–400Hv and gradually go down to the matrix. The surface hardness value of the low carbon steel in the usual sulfnitriding in molten salt as shown in Fig. 6 is much lower than that of the plasma-sulfnitrided steel and the thick FeS layer formed on the steel surfaces^[3]. High hardness value at the surface in the present study may be due to Mo solved in sulfnitriding layer and thin FeS layer.

Fig. 7 shows relations between the surface hardness and the compound layer thickness of the steel plasma-sulfnitrided in the gap of 6mm. When treating temperature was increased from 723 to 823K, The surface hardness was increased. The surface hardness of the steel plasma-sulfnitrided at 823K had the highest value and the thickest compound layer. The hardness of thin compound layer is low in the Fig. 7 generally.

The results in 1–3 show as the following

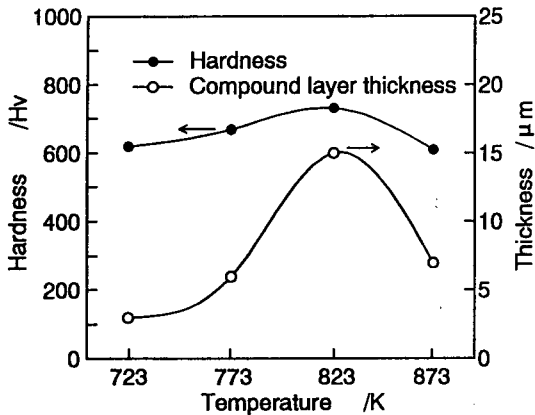


Fig. 7 Relations between surface hardness and compound layer thickness for SCM435 plasma-sulfnitrided vs sulfnitriding temperature in the gap of 6mm.

things. MoS_2 of the subsidiary cathode is sputtered and decomposed by ion-bombarding. The sputtered and decomposed atoms move to the steel of the main cathode repeating collision with gas molecules and deposit on the steel surface, so that the steel is sulfnitrided by combination of ion-nitriding and sputtering of MoS_2 .

CONCLUSIONS

In order to plasma-sulfnitride the steel by combining ion-nitriding of the steel and sputtering of MoS_2 , the steel of SCM435 and MoS_2 plates set parallelly with a small gap and applied negative electric potential to generate hollow cathode discharge in the gap. The results obtained were summarized as follows.

1) Compound layer of 8–15 μm and nitrogen diffusion layer of about 400 μm were formed on the surface of the plasma-sulfnitrided steel.

2) The compound layer consists of FeS containing Mo and iron nitrides. The nitrides of $\epsilon\text{-Fe}_{2-3}\text{N}$ and $\gamma\text{-Fe}_4\text{N}$ were formed under the FeS.

3) The compound layer thickness and surface hardness are different with the gaps between two cathodes in the same sulfnitriding temperature.

4) The surface hardnesses after plasma-sulfnitriding distribute from 640 to 830Hv. The hardnesses of nitrogen diffusion layers distribute mainly 600–400Hv and decreased to the matrix gradually.

5) The surface hardness was higher in plasma-sulfnitriding than usual sulfnitriding in molten salt. This may be due to Mo in sulfnitriding layer.

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