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FORMATION OF IRON SULFIDE BY PLASMA-NITRIDING USING SUBSIDIARY CATHODE

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ABSTRACT

Chromium-Molybdenum steel was plasma-nitrided at 823 K for 10.8 ks in an atmosphere of 30% N₂-70% H₂ gas under 665 Pa without and with a subsidiary cathode of MoS₂ to compare ion-nitriding and plasma-sulfnitriding using subsidiary cathode.

When the steel was ion-nitrided without MoS₂, iron nitride layer of 4μm and nitrogen diffusion layer of 400μm were formed on the steel. A compound layer of 15μm and nitrogen diffusion layer of 400μm were formed on the surface of the steel plasma-sulfnitrided with subsidiary cathode of MoS₂. The compound layer consisted of FeS containing Mo and iron nitrides. The nitrides of ε-Fe₂₃N and γ-Fe₄N formed under the FeS. The thicker compound layer was formed by plasma-sulfnitriding than ion-nitriding. In plasma-sulfnitriding, the surface hardness was about 730 Hv. The surface hardness of the steel plasma-sulfnitrided with MoS₂ was lower than that of ion-nitrided without MoS₂. This may be due to the soft FeS layer formed on the surface of the plasma-sulfnitrided steel.

INTRODUCTION

When a negative electric potential is applied to a steel under low pressure atmosphere of nitrogen-hydrogen mixing gas, low temperature plasma generates near the steel of a cathode. The steel is heated by bombardment of positive gas ions which are accelerated by strong electric field near the cathode^[1]. The steel is nitrided by nitrogen diffusion and then is hardened by both iron nitride and nitrogen diffusion layer. This treatment is called plasma/ion-nitriding^[2-4] and used to improve mechanical and chemical properties such as wear, fatigue and corrosion resistance of steel.

If soft iron sulfide layer is formed on the steel, the layer is effective to provide the fretting friction characteristic to the steel^[5-7]. If a MoS₂ plate is placed parallel to a steel plate in the reduced nitrogen-hydrogen mixing gas atmosphere and a negative electric potential is applied to them, the surface of the steel and MoS₂ will be fastly heated and sputtered by bombardment of the positive gas ions which are increased by hollow cathode discharge effect. Fe, Mo and S atoms sputtered from the two plates of cathodes react with nitrogen, and iron sulfide and nitride can be formed on the surface of the steel. About 10% of the sputtered atoms may also move to the opposite surface through the plasma re-

gion in a d.c. glow discharge^[8]. Thus, plasma-sulfnitriding using the subsidiary cathode of MoS₂ was carried out. Investigations of the sulfnitrided steel were focused mainly on the characterizations of the surface morphology and cross-sectional microstructure^[9].

EXPERIMENTAL PROCEDURE

The samples for nitriding and sulfnitriding were used Cr-Mo steel which includes 0.33% C, 0.23% Si, 0.72% Mn, 0.014% P, 0.013% S, 1.07% Cr and 0.15% Mo. The steel was quenched into water after it was kept at 1123 K for 3.6 ks. The quenched steel was tempered at 873 K for 3.6 ks. The steel was cut to 12mm×10mm×5mm. Prior to nitriding, 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.

Fig.1 shows a plasma-nitriding apparatus. The apparatus has a cathode and anode which are a sample holder and reaction chamber wall respectively. A sulfnitriding sample of Cr-Mo steel called a main cathode was put on the sample holder. MoS₂ called a subsidiary cathode was set parallel to the sample with a gap of 6mm. The size of the MoS₂ is 12 mm×10mm×5mm. After setting the sample and MoS₂, the reaction chamber was evacuated

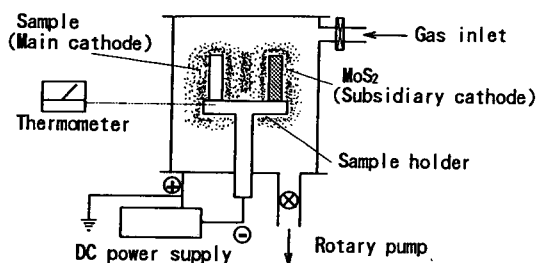


Fig. 1 Schematic drawing of plasma-sulfnitriding apparatus.

under 1.33×10^{-1} Pa. First, the surfaces of the sample and MoS₂ were sputtered to clean for about 1.2 ks in a dc glow discharge in the reduced H₂ gas^[10]. After the sample and MoS₂ were cleaned, the reaction chamber was re-evacuated under 1.33 Pa and then the sample was d.c. plasma-sulfnitrided at 823 K for 10.8 ks in an atmosphere of 30% N₂-70% H₂ mixed gas at 665 Pa. The experimental conditions for plasma-sulfnitriding are shown in Table. Discharge voltage was controlled at about 400 V. The steel was also ion-nitrided without MoS₂ under same conditions. The temperature of the sample was measured with a chromel-alumel thermocouple embedded in the sample holder.

Chemical components of surface layers of the plasma-nitrided steel were analyzed with EDX. The formed precipitates were identified by x-ray diffraction using Co-K α . Surface morphology and cross-sectional structure were observed by a scanning electron microscope and an optical microscope. Hardness was measured by loading 100 g for 30 s with micro-Vickers hardness tester.

Table 1. Experimental conditions for plasma-sulfnitriding with MoS₂

Gas pressure*	665Pa
Treatment time*	10.8ks
Ratio of N ₂ /H ₂ *	3/7
Sample temperature*	832K
Gap between sample and MoS ₂	6mm
Discharge current	0.25A

* This is used as experimental conditions for ionnitriding without MoS₂, too.

RESULTS AND DISCUSSION

Fig. 2 shows dependence of discharge current on gas pressure when the sample plasma-nitrided without and with a subsidiary cathode. Using a subsidiary cathode, sample temperature and discharge current were higher than without the subsidiary cathode. When gas pressure increased, a light in the gap between the main and subsidiary cathode was weakened and discharge current value was

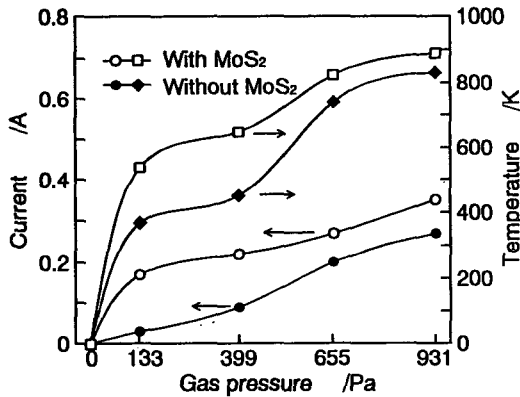


Fig. 2 Dependence of discharge current on gas pressure between without and with a subsidiary cathode (Ratio of $N_2/H_2=3/7$, discharge voltage = 400V, gap = 6mm)

increased slowly. Plasma treatment using the subsidiary cathode is also good for energy savings and energy efficiency^[11].

Fig.3. shows the EDX spectra for the plasma-nitrided sample. Only Fe peak was observed on the sample ion-nitrided without MoS_2 . Mo and S peaks were detected on the sample plasma-sulfnitrided with MoS_2 . It can be seen that Mo and S atoms which sputtered and/or thermally decomposed from MoS_2 reached on the surface of the sample traveling through plasma region between the sample and MoS_2 and then deposited on the sample surface.

Fig.4 shows x-ray diffraction patterns of the sample plasma-nitrided at 823 K for 10.8 ks in a 30% N_2 -70% H_2 mixing gas at 665 Pa. The peaks of α -Fe and γ' - Fe_4N were observed from the surface of the sample ion-nitrided without MoS_2 . On the other hand, the peaks of FeS and ϵ - $Fe_{2-3}N$ were detected at the same angle of 51.5 degree from the surface of the sample plasma-sulfnitrided with MoS_2 though the separation of FeS and ϵ - $Fe_{2-3}N$ peaks is difficult because of overlapping of these peaks.

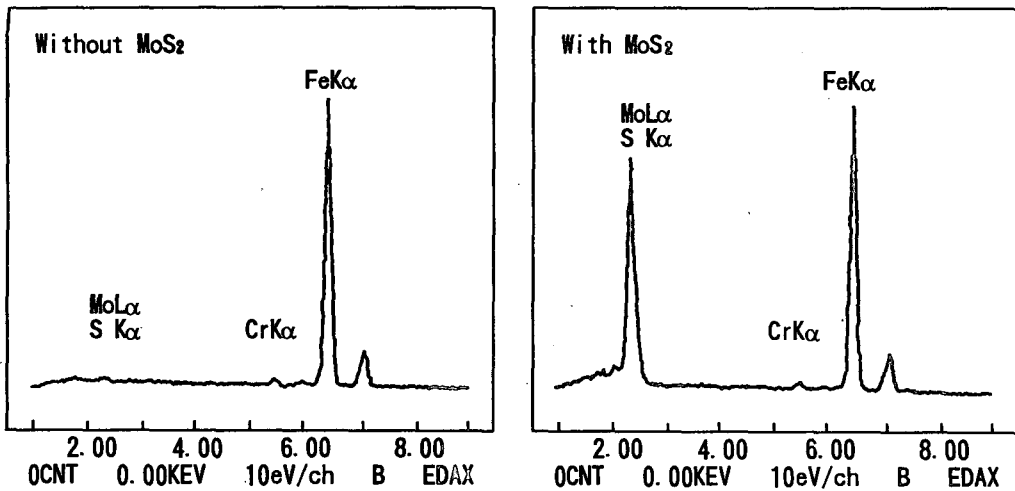


Fig. 3 EDX spectra of the plasma-nitrided sample.

The heights of these peaks are very high compared with the surface of the sample ion-nitrided without MoS_2 , so FeS phase may be formed on the sample plasma-sulfnitrided with MoS_2 from the above EDX results. This means that the Mo and S atoms sputtered from MoS_2 move to sample of opposite cathode and deposit on the sample surface and

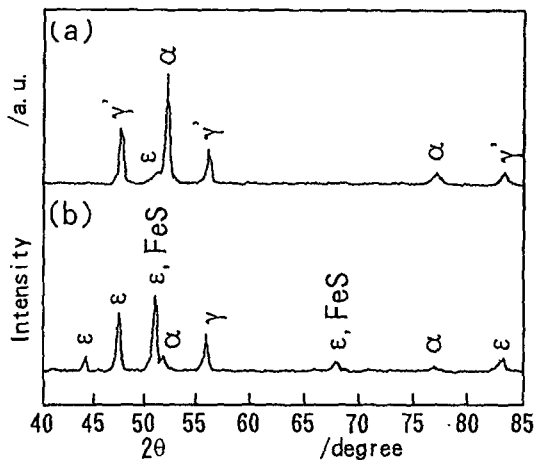


Fig. 4 X-ray diffraction patterns of the plasmanitrided sample (ϵ : $\epsilon\text{-Fe}_{2-3}\text{N}$, γ' : $\gamma'\text{-Fe}_3\text{N}$, FeS, α : $\alpha\text{-Fe}$)
 (a) Ion-nitrided without MoS_2
 (b) Plasma-sulfnitrided with MoS_2

then FeS layer, which is thermodynamically stable, is formed on the sample surface. When sample temperature is 823 K, the diffusion coefficients of N, Mo and S atoms are calculated as 4.501×10^{-8} , 2.915×10^{-14} and $1.893 \times 10^{-13} \text{ cm}^2/\text{sec}$ respectively. The diffusion coefficients of Mo and S atoms in $\alpha\text{-Fe}$ are much smaller than that of nitrogen, so Mo and S are difficult to be diffused inside the steel.

Fig.5(a) shows SEM image of the sample ion-nitrided without MoS_2 . The surface was covered with coarse precipitate. The precipitate is iron nitrides of $\epsilon'\text{-Fe}_2\text{N}$ and $\epsilon\text{-Fe}_{2-3}\text{N}$ as shown in Fig.4.

Fig.5(b) shows SEM image of the sample surface plasma-sulfnitrided with MoS_2 . The surface of the plasma-sulfnitrided sample was roughened and covered with fine precipitate. The precipitate is to form FeS layer containing Mo from results of S detected in Fig.3 and FeS phase detected in Fig.4.

Fig.5(c) shows SEM image of MoS_2 surface exposed in a glow discharge for 10.8 ks in the gap of 6mm. The surface was covered with fine grain-like precipitates. The Mo and

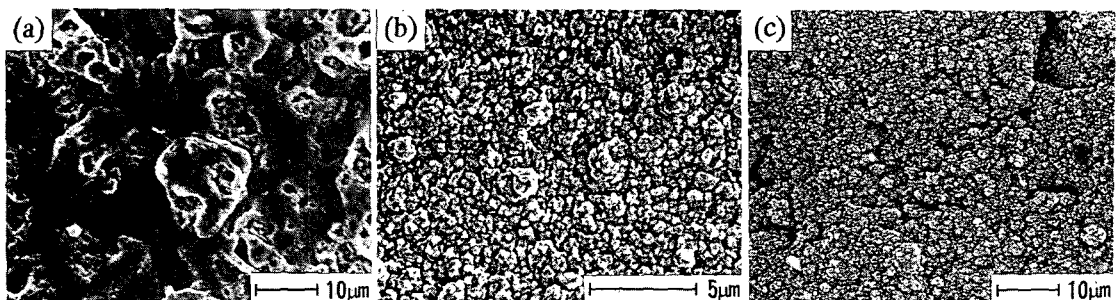


Fig. 5 SEM images of sample plasma-nitrided without and with MoS_2 , and MoS_2 surface.
 (a) Ion-nitrided without MoS_2
 (b) Plasma-sulfnitrided with MoS_2
 (c) MoS_2 exposed in a glow discharge for 10.8ks at 823 K in the gap of 6mm

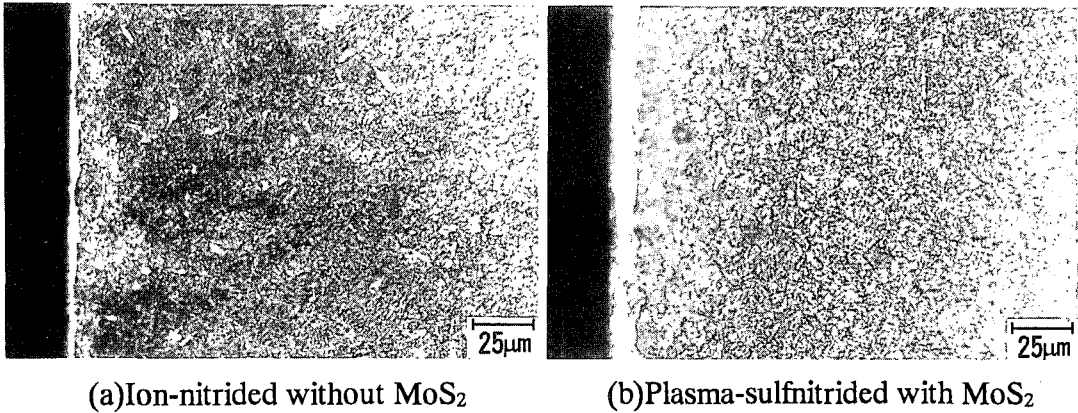


Fig. 6 Cross-sectional micrographs of sample plasma-nitrided without and with MoS₂

S atoms sputtered and/or evaporated from MoS₂ are re-deposited on the same MoS₂ surface after repeating corrosion with gas atoms. In x-ray diffraction analysis, Mo nitride was not detected from the MoS₂ surface and only the height of MoS₂ peak was decreased.

Fig.6 shows cross-sectional micrographs of the plasma-nitrided sample. All the samples were etched for 3 sec with 3% nital10.8ks at 823K in the gap of 6mm

A nitride layer of about 4mm was formed on the sample ion-nitrided without MoS₂. The surface of the sample plasma-sulfnitrided with MoS₂ was covered with a white layer of approximately 15mm thick. The top part of the white layer was made of FeS containing Mo. The iron nitrides of ϵ -Fe₂₋₃N and ϵ' -Fe₂N were formed under the FeS layer as seen from the results of the x-ray diffraction analysis. The thicker compound layer was formed by plasma-sulfnitriding with than without MoS₂ as seen in Fig.6.

Fig.7 shows hardness distributions of the sample plasma-nitrided without and with

MoS₂. The hardness changes from surface to about 400 mm thick were almost same though the hardness of the diffusion layer was generally low. The surface hardness after plasma-sulfnitriding with MoS₂ was lower than after ion-nitriding without MoS₂. This may be due to the soft FeS layer formed on the surface of the plasma-sulfnitrided sample. Because of the thick compound layer of the FeS and iron nitrides, amount of nitrogen diffused inside sample is a little small.

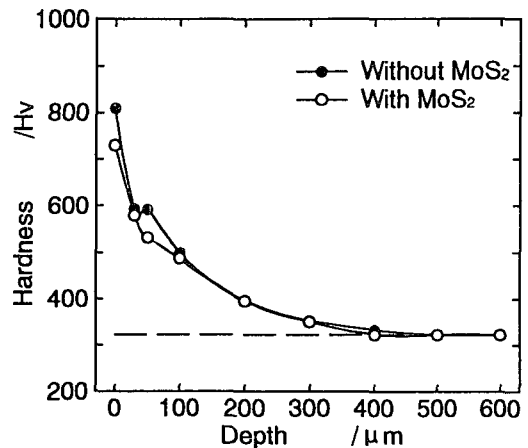


Fig. 7 Hardness distributions of sample plasmanitrided without and with MoS₂

CONCLUSIONS

The sample was plasma-nitrided without and with subsidiary cathode of MoS₂. The following conclusions were obtained.

1) Iron nitride layer of 4 μ m and nitrogen diffusion layer of 400 μ m were formed on the sample ion-nitrided without MoS₂.

2) A compound layer of 15 μ m and nitrogen diffusion layer of 400 μ m were formed on the surface of the sample plasma-sulfnitrided with MoS₂. The compound layer consisted of FeS containing Mo and iron nitrides, where the nitrides of e-Fe₂₋₃N and g'-Fe₄N formed under the FeS.

3) The compound layer after plasma-sulfnitriding was thicker than after ion-nitriding. The surface hardness in plasma-sulfnitriding was about 730 Hv and decreased toward the base slowly.

4) The surface hardness after plasma-sulfnitriding with MoS₂ was lower than after ion-nitriding without MoS₂. This may be due to the soft FeS layer formed on the surface of the plasma-sulfnitrided sample.

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