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TiN 코팅된 SKD11과 SKD61의 내마모 성질에 미치는 이온주입 효과

장태석, 이수완, 문대원*, 방건웅*

선문대학교 재료금속공학부, *한국 표준 연구원

Effect of ion implantation on the tribological properties of TiN-coated SKD 11 and SKD 61

T. S. Jang, S. W. Lee, D. W. Moon*, and G. W. Bahng*

Division of Metallurgical and Materials Engineering, Sun Moon Univ.
* Materials Evaluation Center, KRISS, Korea

Abstract

To figure out whether the tribological properties of a hard-coated layer can be improved by ion implantation, TiN-coated SKD 11 and 61 were implanted with nitrogen ion and their wear properties were examined systematically. The amount of nitrogen ions implanted on the coated layer was 2×10^{15}, 10^{16}, 10^{17}, and 10^{18} ions/㎠, respectively. X-ray diffraction revealed the intensity of the peaks belong to TiN tended to increase as the ion dose increased, which implied that the implantation promoted the formation of TiN in the coated layer. However the hardness of the specimens increased then decreased again as the ion dose increased, resulting in a obvious drop of the hardness for the ion dose of 2×10^{18} ions/㎠. While the adhesion of the coated layer of SKD 61 was excellent regardless of the implantation, the adhesion of the layer of SKD 11 was apparently improved by the implantation. The overall wear properties of SKD 11 was better than that of SKD 61, and the best result was yielded at the ion dose of 2×10^{15} ions/㎠.

1. INTRODUCTION

Ion implantation is an important technique for semiconductor fabrication because the physical properties of a semiconductor can be modified more rapidly and more precisely by the technique. But it can be also applied to improve the tribological properties of the surface of an engineering material because the mechanical properties of the material can also be modified by the technique. Many works in reality have been carried out to improve overall mechanical properties against corrosion, high temperature oxidation, fatigue, impact, wear, etc. by implanting some ions into the surface area of tool steels[1]. Except for the wear properties of such metals as carbon steel, stainless steel, aluminium alloys, copper alloys, nickel alloys, and titanium alloys[2], the wear properties of polymers[3] and ceramics[4] can also be enhanced by the ion implantation. From these works it has been proved that the life time of ion-implanted components is extended considerably.

On the other hand improvement of tribological properties of various engineering components by hard coatings like TiN, TiC, and TiCN on the components has greatly attracted lately in the industrial and research sectors. This can be attributed to the excellent wear, corrosion, and frictional properties of these coatings under extreme application conditions. Among the coatings TiN is the most widely used one in commercial. Although TiN is such widely coated on many engineering parts, a systematic study to prolong their life time has not been well executed. Furthermore no work has been performed how the implantation affects the wear properties of TiN-coated layer when nitrogen ions were implanted on the layer. In this study, therefore, as an effort to extend the lifetime of the components using at severe working conditions, TiN-coated materials were implanted with nitrogen ion and examined their wear properties to find out whether the implantation can improve the tribological properties of the hard-coated materials.

2. EXPERIMENTS

Commercially available SKD 11 and SKD 61 were machined to disc-type (ϕ25mm $\times$t 4mm) specimens. The chemical compositions of these materials can be found in the reference[5]. Heat treatment of the specimens was carried out by the conventional heat treatment procedures[5]. The average value of hardness of SKD 11 after heat treatment was 61 HRC, while that of SKD 61 was 51 HRC. After heat treatment the disc specimens were ground to a surface finish less than 0.5 μm. Then they were cleaned ultrasonically in acetone for about 10 minutes and rinsed with alcohol.

TiN coating of the specimens was done by RF magnetron sputtering. Prior to TiN coating, the specimens were RF etched in Ar atmosphere under the vacuum of 5×10^{-3} torr. Then thin Ti layer was deposited first followed by the deposition of TiN at the vias voltage of -80 V under the vacuum of 4.3×10^{-3} torr. Final coating of TiN was done at the vias voltage of -120 V. After TiN coating the coated layer of the specimens was implanted by nitrogen ion using 200 keV ion implanter. The ion energy was 100 keV. The current density were 200 A/cm^2 for the ion dose of 2×10^{15} and 2×10^{16}, 160 A/cm^2 for 2×10^{17}, and 250 A/cm^2 for 2×10^{18} ions/cm^2, respectively. It was found that the color of the specimen surface changed from gold to brown as the amount of ion dose increased.

Implanted specimens were examined by XRD (Cu Kα, λ=0.15405 nm) to investigate the effect of the implantation on the phase changes in the coated layer. Variation of hardness of the specimens was measured by micro Vickers hardness tester with the applied load of 10 gf. To measure the adhesion of the coated layer to the substrate and the changes of the adhesion by the implantation, scratch test (REVE-TEST, CSEM Co.) was employed. The load applied on a specimen during the test was increased from the initial 100N to the final 200N with the loading velocity (dL/dt) of 100 N/min and the transporting rate (dx/dt) of 10 mm/min. Failure of a coated layer occurred at a critical load (Lc) was detected by an acoustic detector. The wear and friction test were conducted for one hour in air utilizing a reciprocal ball-on-disc type test machine (Cameron Plint TE77). The load applied on a specimen was 10 N and the sliding speed was fixed at 1 Hz throughout the sliding distance of 10 mm. The loading balls were made of bearing steels. Changes of friction coefficient were obtained from the test. The wear volume was calculated by measuring the weight change of a specimen before and after the test. The shape of wear tracks was observed by SEM.

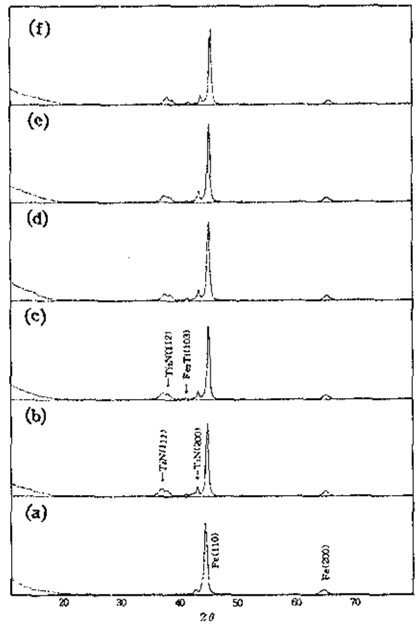


Fig. 1 X-ray reflections obtained from SKD 11 (a) before TiN coating, (b) after TiN coating only, and after nitrogen-ion implantation with the ion dose of (c) 2×10^{15}, (d) 2×10^{16}, (e) 2×10^{17}, and (f) 2×10^{18} ions/cm².

3. RESULTS and DISCUSSION

Fig. 1 and 2 shows the X-ray reflections obtained from the specimens of SKD 11 and SKD 61, respectively. In every case, strong reflections were observed from Fe (110) and Fe (200).

For SKD 11, weak reflections which seemed to be attributed to the formation of Fe-Cr compound were also observed at $2\theta=\sim42.6°$ and 50°. After the TiN coating of SKD 11 (Fig. 1b) not only TiN (111) and TiN (200) were clearly observed, but also Ti_2N (112) was observed. It tells us that small amount of Ti_2N is also formed with TiN by the coating. Altho-

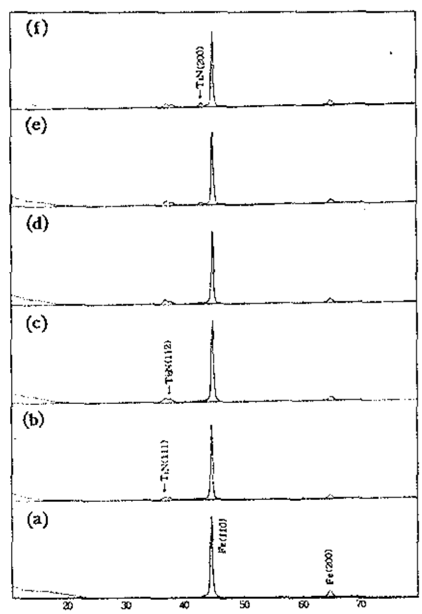


Fig. 2 Same as Fig. 1, for SKD 61.

ugh no obvious change of the diffraction pattern was observed after ion implantation, intensities of TiN peaks tended to increase as the amount of nitrogen-ion dose increased. It implies that the region of TiN in the coated layer is extended by the implantation.

Broad peaks observed at $2\theta=35\sim38°$ are thought to be related to the wide homogeneity range of TiN[6]. The specimens of SKD 61 show simpler diffraction patterns, without revealing the reflections of Fe_2Ti or Fe-Cr. After implantation, the intensity of TiN (200) increased with the increase of the amount of nitrogen-ion dose, telling us the promotion of TiN in the coated layer by the implantation.

Fig. 3 shows the average values of hardness of the TiN coated and then nitrogen-ion implanted layers. As shown in the figure, hardness of the surface area generally increases after implantation. For the specimens of SKD 11 the increase of hardness showed its peak at the ion dose of 2×10^{16} ions/㎠, while that

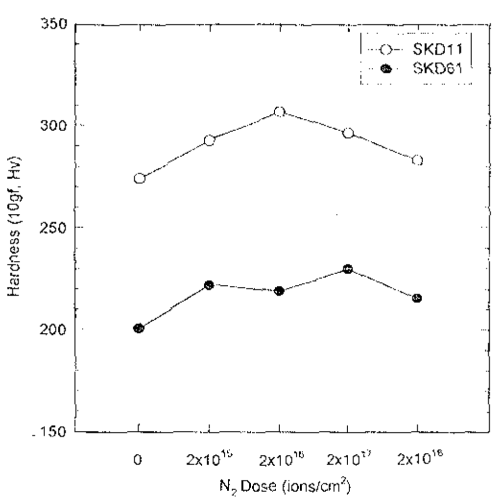
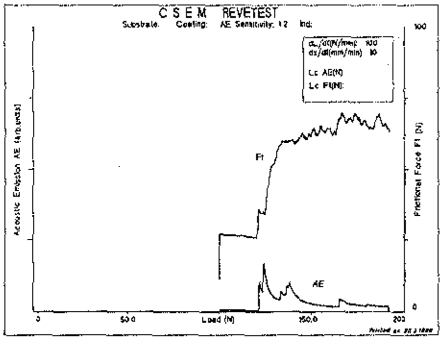


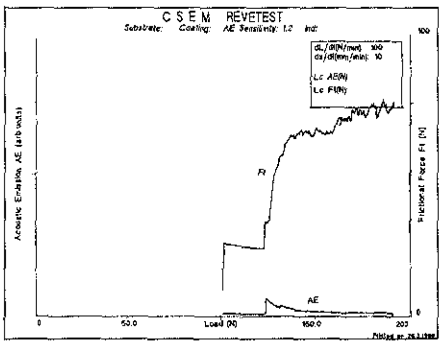
Fig. 3 Variation of hardness with the variation of dose rate of nitrogen ions.

of the SKD 61 occurred at the ion dose of 2×10^{17} ions/㎠. At the ion dose of 2×10^{18} ions/㎠, hardness of both specimens were obviously decreased. Therefore, implantation of excessive amount of nitrogen ions is not effective to improve the surface hardness. The up and down of the hardness occurring by the implantation is thought to be due to the mutual reaction of several factors such as solution hardening on the implanted surface, dispersion of nitrides, and formation of defects like vacancy and dislocations during implantation[7, 8].

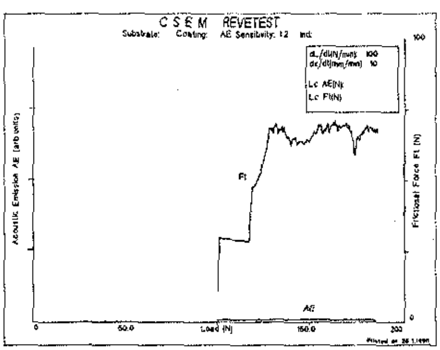
Fig 4 and 5 show the results of scratch tests performed to figure out how ion implantation affects the adhesion of the coated layer to the substrate. In the case of unimplanted SKD 11, as shown in Fig. 4a, double peaks of friction force (Ft) and acoustic emission (AE) coincide at around 125 N. It tells us that, although the second layer was very thin, the coated layer was actually consisted of double layers and they exfoliated almost at the same time. After implantation, however, thickness of the second layer decreased as the amount of nitrogen-ion dose increased as shown in Fig 4b and 4c. Eventually the second layer decreased almost completely at the ion dose of 2×10^{18} ions/㎠. At the same time, the adhesion of the layer was also improved when the amount of ion dose is more than 2×10^{17} ions/㎠. During implantation, high-energy nitrogen ions colliding into the TiN-coated layer provide the thermal energy which promotes atomic diffusion and chemical reaction in the layer. This promotion eventually enhances the intermixing effect[9], yielding a transition from the double layer to the monolayer and the impro-



(a)

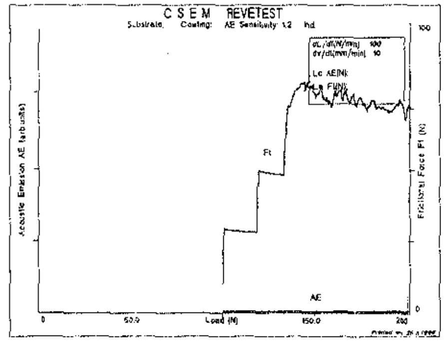


(b)

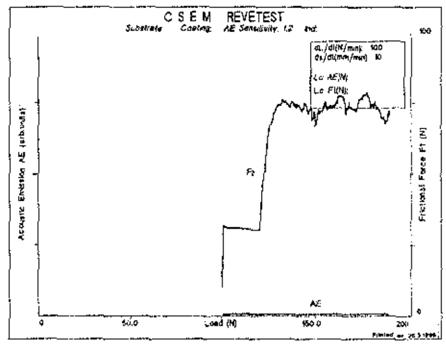


(c)

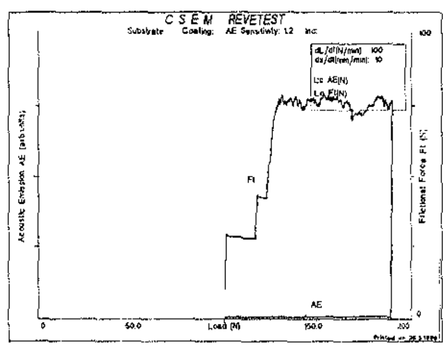
Fig. 4 Variety of scratch test obtained from SKD 11 coated with TiN followed by the nitrogen-ion implantation with the ion dose of (a) 0, (b) 2×10^{15}, and (c) 2×10^{17} ions/cm².



(a)



(b)

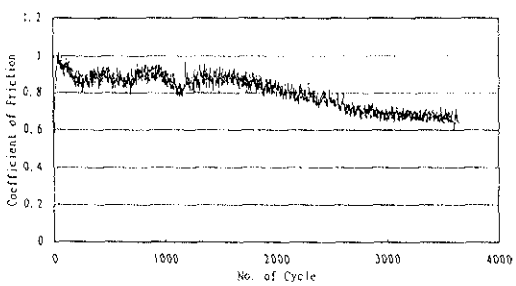


(c)

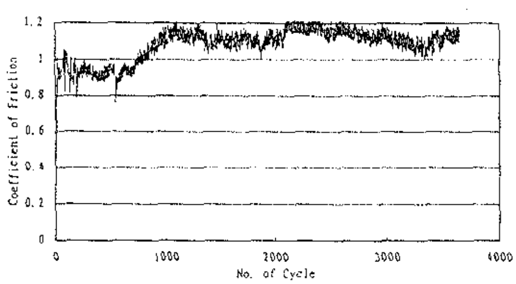
Fig. 5 Same as Fig. 4, for SKD 61.

vement of the adhesion. Unimplanted SKD 61, as shown in Fig. 5a, clearly shows abrupt jump of friction force at about 120 N and 130 N, revealing an obvious formation of double layers. However, acoustic emission dose not show any change, telling us that the adhesion of the layer to the substrate is excellent. Regardless of ion implantation, the adhesion of the coated layer was excellent for the specimens of SKD 61. But the change in the formation of the layers due to the nitrogen-ion implantation was more obvious as shown in Fig. 5b and 5c.

The changes of friction coefficient of the TiN-coated and then nitrogen-ion implanted SKD 11 and SKD 61 are compiled in Fig. 6 and 7, respectively. Friction coefficient of the specimens implanted with the ion dose of 2×10^{16} and 2×10^{18} ions/cm² in each case showed similar variation to those of the specimens implanted with the ion dose of 2×10^{17}. In all specimens friction coefficient instantaneously increased at the beginning of the test. For SKD 11, friction coefficients generally in

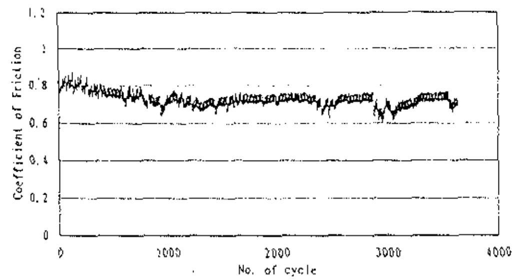


(a)

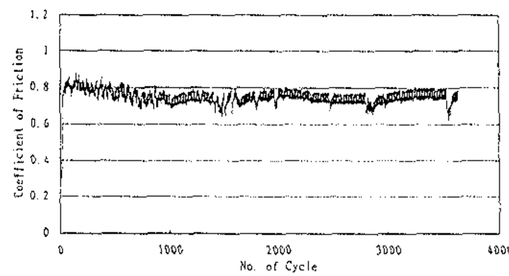


(b)

Fig. 6 Changes in friction coefficient of the TiN-coated SKD 11 after nitrogen-ion implantation with the ion dose of (a) 2×10^{15} and (b) 2×10^{17} ions/cm². Friction coefficient of the specimens implanted with the ion dose of 2×10^{16} and 2×10^{18} ions/cm² varied similarly to that of the one with 2×10^{17} ions/cm².



(a)



(b)

Fig. 7 Same as Fig. 6, for SKD 61.

creased as the tests were proceeded except for the specimen implanted with the ion dose of 2×10^{15} ions/cm². In general, as the friction between the test ball and the specimen continues, the coated layer wears out and exfoliates resulting in the formation of considerable amount of debris. Then the debris may adhere to the test ball causing an adhesive wear or be deformed plastically by the ball. It can be the reason of the increase. However, the specimen implanted with the ion dose of 2×10^{15} ions/cm² reveals better wear properties by showing that gradual decrease of friction coefficient throughout the test, which tells us that it was worn out abrasively. The specimens of SKD 61 showed relatively simpler changes in friction coefficient as show in Fig. 7. Except the abrupt increase of the coefficient at the beginning of the test, friction coefficients were at steady state or they gradually decreased as the tests were proceeded.

The variation of friction coefficient just mentioned above implies that the wear properties of SKD 61 would be better than those of SKD 11. SEM observation of the wear tracks, however, does not support it. Fig. 8 and 9 show the wear tracks of TiN-coated and then nitrogen-ion implanted SKD 11 and 61, respectively. Before implantation, the wear track of the SKD 11 was much smaller than that of the SKD 61, producing less amount of wear debris (not shown in this paper). In general, high enough hardness of the coated layer and the substrate and the superior adhesion of the layer to the substrate are prerequisite to the excellent wear properties of a coated material[10]. But, as revealed in Fig. 3, hardness of SKD 11 is higher than that of SKD 61. Therefore, even though the adhesion of the coated layers of SKD 61 is superior to that of SKD 11, overall wear properties of SKD 11 are better than those of SKD 61. The difference of the overall wear properties of the two is expected to carry over to the implanted specimens as it is. Fig. 8 and 9 tell us that the wear behavior of the specimens was relatively complicate, usually accompanying adhesive wear with

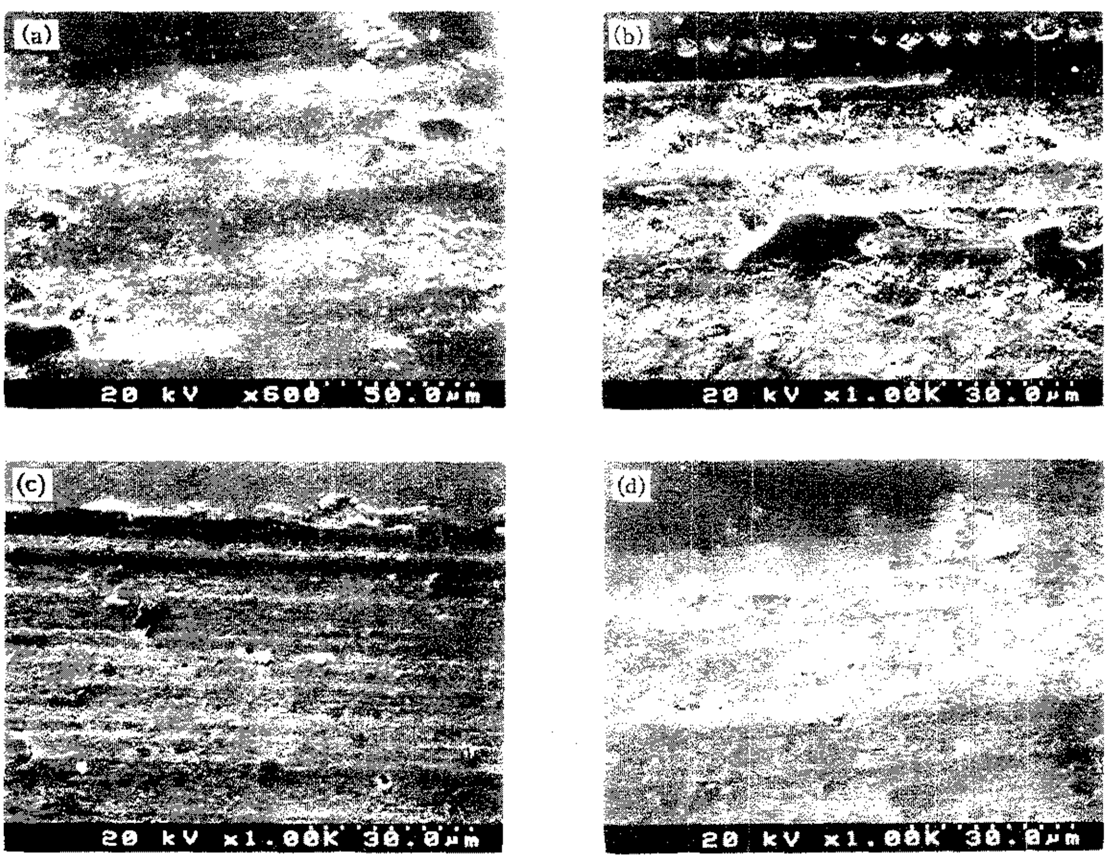


Fig. 8 SEM micrographs of wear tracks formed on SKD 11 coated with TiN followed by the nitrogen-ion implatation with the ion dose of (a) 2×10^{15}, (b) 2×10^{16}, (c) 2×10^{17}, and (d) 2×10^{18} ions/cm^2.

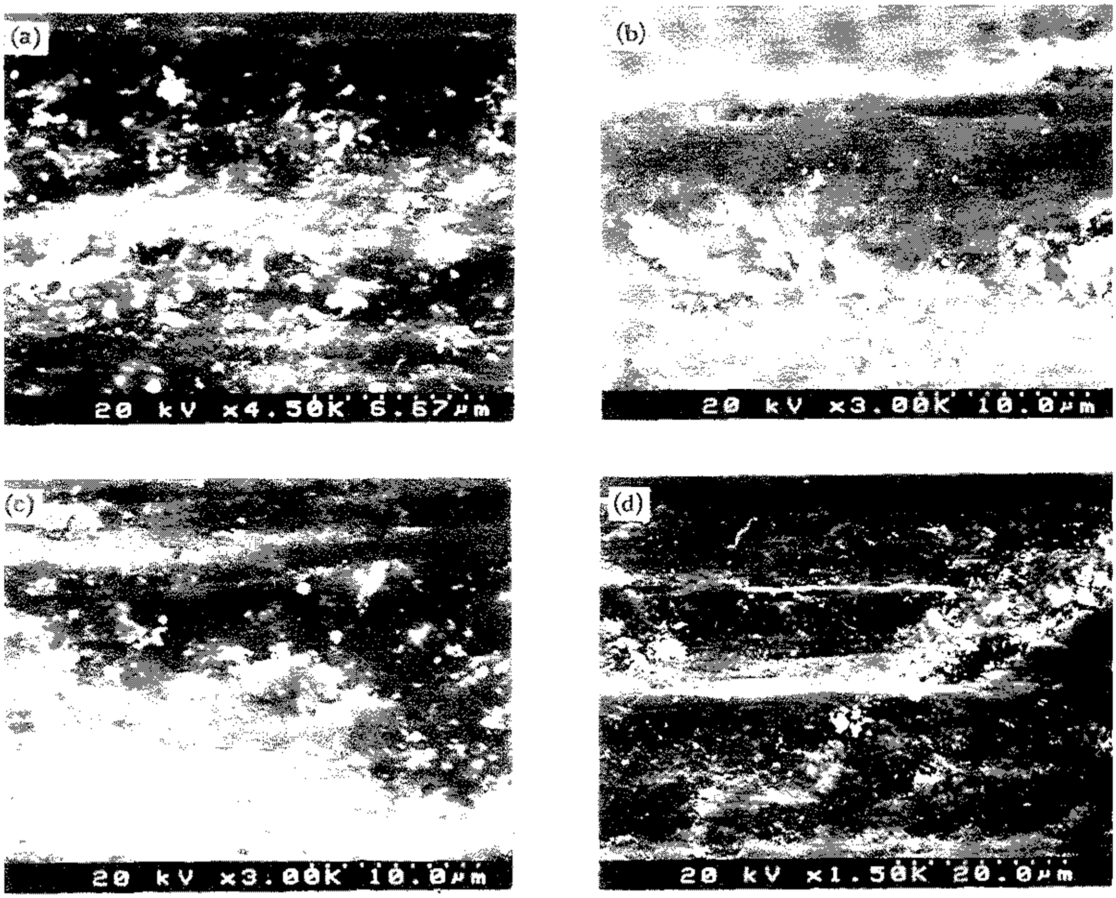


Fig. 9. Same as Fig. 8, for SKD 61.

abrasive wear. It can be seen that specimens in Fig. 8a, 9a, and 9c were mainly worn out abrasively, while the others were worn out adhesively. Agglomeration and plastic deformation of wear debris are clearly shown in the central region of Fig. 8b. Delamination of the coated layer is also clearly seen in the upper part of the figure. Brittle fracture and delamination of the coated layer are thought to be attributed to the inability of the layer (which is inherently brittle) to sustain the same amount of elasto-plastic deformation of the softer substrate experienced during the cyclic loading and unloading process[11]. Fig. 10 shows the variation of weight loss of SKD 11 caused by the wear test. As shown in the figure, the specimen implanted with the ion dose of 2×10^{15} ions/cm^2 yielded the least weight loss. Therefore, the specimen of SKD 11 implanted with the ion dose of 2×10^{15} ions/cm^2 exhibited the best tribological properties even though the results of hardness test, adhesion test, and wear test are not matched consistently.

4. SUMMARY

By XRD it was observed that the peaks belong to TiN tended to increase as the amount

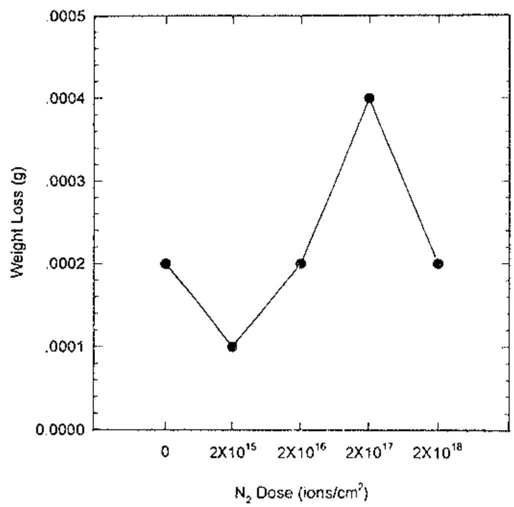


Fig. 10 Variation of wear volume with the variation of nitrogen-ion dose for the TiN-coated SKD 11.

of ion dose increased, which implied the implantation promoted the formation of TiN in the coated layer. The hardness of the specimens tend to increase and then decrease as the amount of ion dose increases, resulting in a obvious drop of the hardness for the ion dose of 2×10^{18} ions/cm². While the adhesion of the coated layer of SKD 61 was excellent regardless of the implantation, the adhesion of the layer of SKD 11 was apparently improved by the implantation. The overall wear properties of SKD 11 was better than that of SKD 61, and the best result was yielded at the ion dose of 2×10^{15} ions/cm².

5. ACKNOWLEDGMENT

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