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Adhesion and wear properties of TiN films deposited on martensitic stainless steel and Stellite by reactive magnetron sputter ion plating

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Abstract

TiN films were deposited onto the turbine blade materials, AISI 403 martensitic stainless steel and Stellite 6B, using reactive magnetron sputter ion plating. The hardness of the TiN film increases with the residual compressive stress and has a maximum value of 3400 kg/mm^2 at the substrate bias of about -75 V. In the scratch adhesion test, the critical loads for cohesive failure and adhesive failure are sensitively governed by the film hardness. The wear rate decreases with increasing hardness and has a minimum value at about -75 V. The ion plated TiN has a superior wear resistance than the bare Stellite 6B and AISI 403 martensitic stainless steel. © 1998 Elsevier Science B.V.

1. Introduction

Erosion of steam turbine blades, especially low pressure ones, in nuclear power plants has been a significant problem throughout steam turbine history in terms of turbine performance, efficiency, safety and life time. The erosion occurred by the collision of water drops in steam with rotating blades operating at high speeds. As an effort to solve the erosion problem, erosion resistant materials such as Stellite 6B (Co-base alloy) were brazed on the leading edges of the blades which were subjected to the most significant damage [1–4]. These shield materials, however, were also eroded with the rate higher than desired. Therefore, the development of more erosion-resistant material is needed.

In this study, in order to improve the erosion resistance of the blade material, a high impedance (= density × sound speed) material based on Springer's model [5] was coated. TiN was selected as a coating material because it has high hardness, chemical stability, low friction coefficient, good oxidation and corrosion resistance. In recent years, TiN has been coated with various coating techniques. Of those, ion plating has been known as the most efficient technique which allows an improved mechanical property because the continuous bombardment of the high energy ions and neutrals onto the substrate and the growing film provides the film with high density, excellent adhesion and surface coverage [6]. The substrate bias is the most critical parameter in ion plating because it causes the changes of the crystal structure and morphology of the deposited film. Until now, several investigators have studied the effects of substrate bias on the morphology, composition, hardness and wear resistance of the sputtered TiN films [7–9]. However, their results were not comprehensive and rather unconnected. Therefore, a systematic study is required on the relationship between the substrate bias and the various film properties. In this study, various properties such as structure, composition, residual stress, hardness, adhesion and wear resistance of the TiN films are studied with respect to the substrate bias and the correlations of the mechanical properties are discussed.

2. Experiment

Fig. 1 is a schematic diagram of the reactive magnetron sputter ion plating apparatus. The substrates were AISI 403

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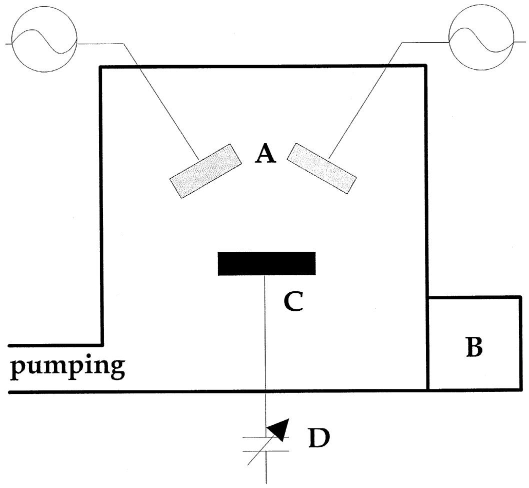

Fig. 1. Experimental apparatus for TiN ion plating; (A) target, (B) load lock system, (C) substrate and (D) dc substrate bias.

martensitic stainless steel and Stellite 6B which are steam turbine blade materials. The substrates were mirror polished to 0.3 μm Al_2O_3 powder, followed by ultrasonic cleaning in ethyl alcohol and acetone and then dried. The prepared specimens were carried into the process chamber using a load–lock system. High purity nitrogen was used as a reactive gas. Prior to film deposition, the Ti target (99.99% purity) and the substrate were sputter-cleaned to remove the oxide and the contaminant layer existing on their surfaces. Details of the deposition conditions are given in Table 1. Thickness of the TiN film was maintained at about 5 μm to avoid the effect of film thickness on the mechanical properties such as adhesion force and wear resistance.

Residual stress of the deposited film was determined by $\sin^2\psi$ method [10] with (220) reflection plane using an X-ray diffractometer. Hardness of the film was measured using a micro Vickers hardness tester (Mitutoyo MVK-H1) with a test load of 10 g. A scratch adhesion tester (CSEM Revetest) was used to evaluate the adhesion force of the TiN film. The test was carried out in a manner that the applied load on the diamond tip (tip radius: 200 μm, conical angle: 120°) is continuously increased, while the tip is moving with a constant speed. The loading rate (dL/dt) and the scratching speed (dx/dt) were 100 N/min and 10 mm/min, respectively. The critical loads for the cohesive and the adhesive failures were determined by investigating the tested surface with an optical microscope. A wear test was performed with a ball-on-disc wear tester (CSEM TRIBOMETER). The ball was SiC of 5.1 mm in diameter which has a Vickers hardness of 4000 kg/mm^2. In order to make a severe wear condition, a dry contact was adopted. The wear test conditions were as follows: an applied load of 10 N, a sliding speed of 1.13 m/min and a sliding distance of 188.5 m (friction radius: 3 mm, number of rotations: 10,000). Wear resistance was determined by measuring the wear track width and the frictional force.

Table 1
Deposition conditions of TiN film

Base pressure	$< 5 \times 10^{-7}$ Torr
Working pressure	6×10^{-3} Torr
Target power	RF 900 W
Deposition temp.	500°C
N_2/Ar	5 sccm/2 sccm
Substrate bias	0– −200 V
Deposition rate	2.5–3 μm/h

3. Results and discussion

3.1. Characterization of TiN film

Fig. 2 shows the typical cross-sectional SEM images of TiN films deposited without and with substrate bias. The

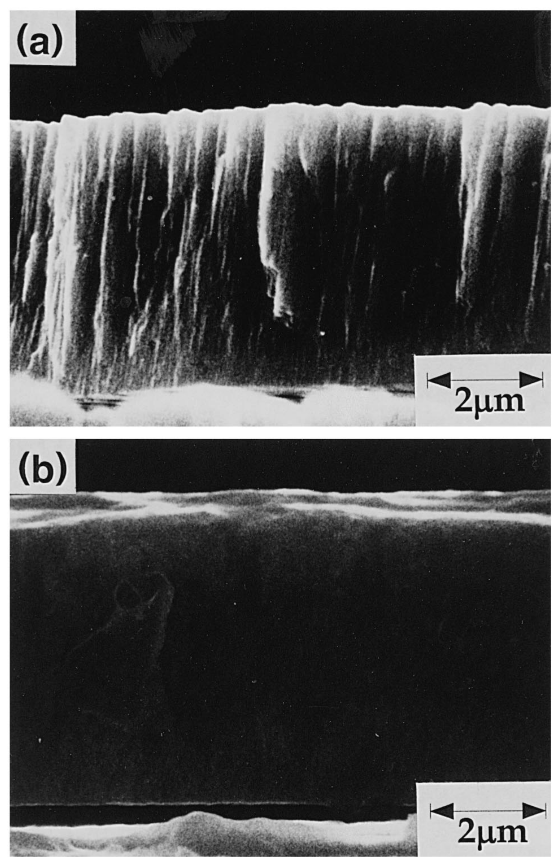

Fig. 2. Cross-section morphologies of TiN films deposited at 500°C, N_2/Ar = 5/2 and target power = 900 W by using SEM; (a) substrate bias = 0 V and (b) substrate bias = −75 V.

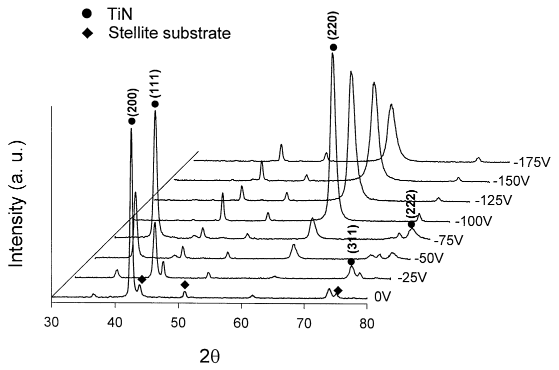

Fig. 3. XRD patterns of TiN films deposited on Stellite with the variation of substrate bias.

microstructure and morphology of the TiN films were sensitively affected by the substrate bias. Without substrate bias, the film had the facet type grains with columnar structure, whereas, with substrate bias the surface of the film became very smooth and the columnar structure disappeared due to the bombardment of energetic ions.

According to composition analysis by Auger electron spectroscopy (AES), the TiN film deposited at zero bias voltage contains a few atomic percent of oxygen and carbon as impurities, but they were effectively removed by applying substrate bias below the detection limit of AES. Since the N/Ti ratios in the deposited TiN films were nearly unity regardless of substrate bias voltage (except at zero bias where the N/Ti ratio was slightly less than unity), the influence of the film composition on the mechanical properties was not considered in this research.

The XRD patterns of TiN films deposited onto Stellite substrates with the variation of substrate bias are shown in Fig. 3. The film produced at zero bias showed (200) preferred orientation. When applying the bias voltage of −25 V, the degree of (200) preferred orientation was reduced with a gradual increase of the (111) intensity. As the substrate bias increased further, the degree of (111) preferred orientation became higher and showed the maximum at the bias voltage of −75 V. However, when applying the bias voltage equal to or greater than −100 V, the (220) reflection plane became dominant. At zero bias voltage, the strain energy term is not important because the energies of ions and atoms bombarding on the growing film are very low. Therefore, the growth of (200) plane, the lowest surface energy plane in TiN crystal [11], is expected to be promoted. As the substrate bias increases, the strain energy becomes dominant due to the ion bombardment, causing the growth of the film with (111) plane, the lowest strain energy plane [11], to be promoted. It is not yet understood, however, why the preferred orientation changed from (111) to (220) above −100 V. At the higher bias voltages above −100 V, (220) peak became smaller and broader with increasing substrate bias, which indicates that the severe bombardment on the growing film by the ions with high energy induced a decrease in film crystallinity and a significant nonuniform strain within TiN lattice.

Fig. 4 represents the linearity of 2θ versus $\sin^2\psi$ as a function of substrate bias for (220) reflection plane using $\sin^2\psi$ method. The residual stresses calculated from Fig. 4 are shown in Fig. 5. As the substrate bias increased, the residual compressive stress increased due to the bombardment of energetic ions. After reaching the maximum at −75–−100 V, it decreased with further increase of the

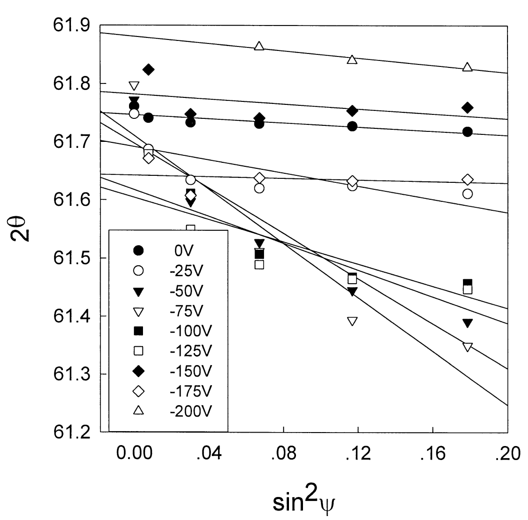

Fig. 4. 2θ versus $\sin^2\psi$ plots for the (220) XRD peaks of TiN films deposited at 500°C, $N_2/Ar = 5/2$ and target power = 900 W with the substrate bias.

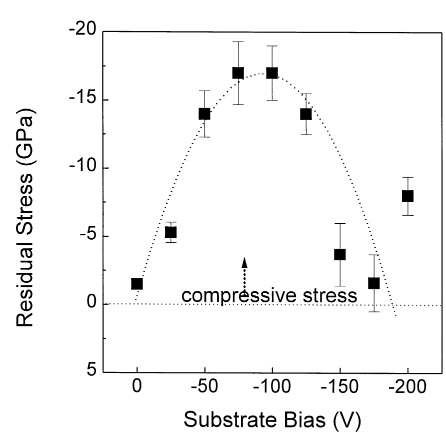

Fig. 5. Variation of residual stress with the substrate bias of TiN films deposited at 500°C, $N_2/Ar = 5/2$ and target power = 900 W.

substrate bias. The increase of the residual compressive stress with the substrate bias up to −75 V agrees with the XRD result that the degree of preferential growth with (111) plane, the lowest strain energy plane, increases with the substrate bias. However, with further increase of the bias, the residual stress decreased through the maximum at −75–−100 V, which seems to be related with the decrease in crystallinity due to the damage in the film by too severe ion bombardment.

3.2. Hardness of TiN film

It is generally known that the Vickers hardness of bulk TiN is 1800–2000 kg/mm^2 but TiN film has a broad range of about 400–3000 kg/mm^2 in Vickers hardness, depending on deposition conditions [12–14]. Fig. 6 represents the micro Vickers hardness of the TiN film as a function of substrate bias. The hardness of the film was 2100 kg/mm^2 at zero bias voltage and increased with the substrate bias. It showed the maximum value of 3400 kg/mm^2 at about −75 V and then decreased. The film hardness is largely influenced by the residual stress. The values of the film hardness (Fig. 6) and those of the residual compressive stress (Fig. 5) are represented in Fig. 7, which shows mutual correlation between them. The increase in film hardness with increasing substrate bias to about −75–−100 V is thought to be due to the densification of the film and increase in the residual compressive stress by the bombardment of ions. However, above this bias, the film was damaged by too severe ion bombardment and thus the residual compressive stress decreased, resulting in the decrease in film hardness. Another factor which can affect the hardness of film is the film orientation. However, it was not possible to distinguish the influence of orientation on the film hardness from that of residual stress.

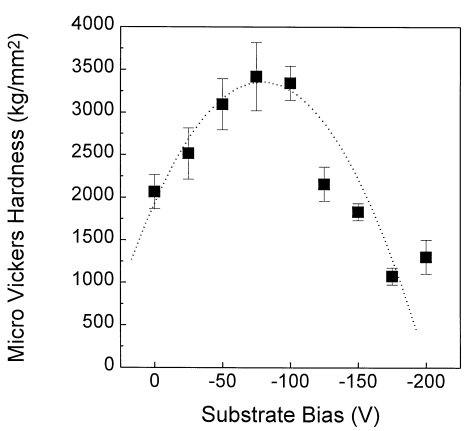

Fig. 6. Variation of micro Vickers hardness with the substrate bias of TiN films deposited at 500°C, $N_2/Ar = 5/2$ and target power = 900 W.

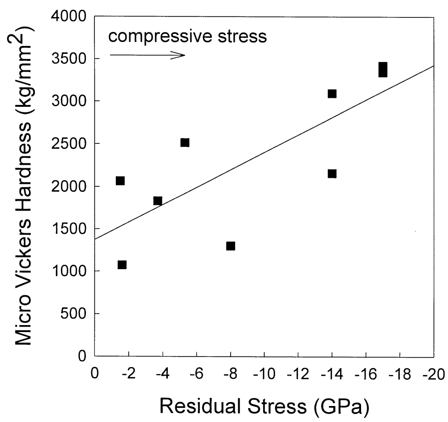

Fig. 7. Residual stress versus micro Vickers hardness plots for TiN films.

3.3. Adhesion force of TiN film

The adhesion force of TiN films deposited with the substrate bias was measured using the scratch adhesion test method. In this study, the adhesion force of the film was classified into two critical loads: one is the critical load required for the failure of the film itself (cohesive failure) and the other is the critical load required for the failure of the interface between the film and the substrate (adhesive failure). In the adhesion test, it is expected that if the interfacial adhesion between the film and the substrate is poor, the cohesive failure and the adhesive failure will occur simultaneously. While, if the interfacial adhesion is strong, the cohesive failure will take place first and then be followed by the adhesive failure. In this case, the critical load for the adhesive failure (L_A) is affected by the critical load for the cohesive failure (L_C). Fig. 8 shows L_C and L_A for the TiN films coated on the martensitic stainless

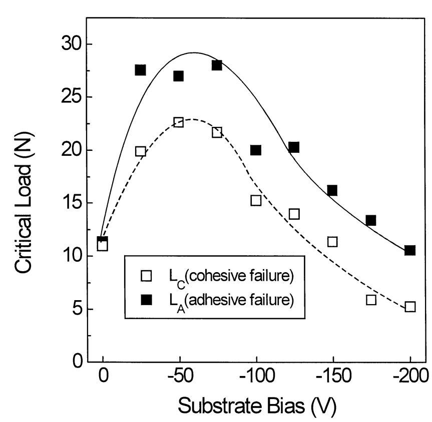

Fig. 8. Variation of critical loads for the TiN films coated on martensitic stainless steel with the substrate bias.

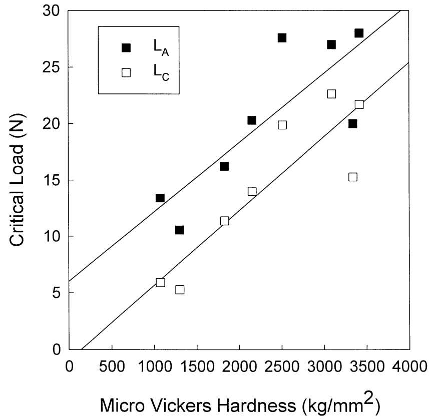

Fig. 9. Micro Vickers hardness versus critical loads plots for cohesive and adhesive failure.

steel substrate as a function of substrate bias. At zero bias voltage, the cohesive and the adhesive failures occurred simultaneously, which implies that the film has a poor adhesion. When biased, the cohesive failure was followed by the adhesive failure, indicating that the film adhesion was improved by applying the substrate bias. L_C and L_A increased with increasing substrate bias and had the maximum values of 22 and 28 N at about −75 V, respectively. With further increase of the substrate bias, however, both L_C and L_A decreased. Fig. 9 represents the relation between the critical loads and the film hardness. The critical load for the failure of the film itself, L_C, shows a linear relation with the film hardness. Once the failure of the film itself occurs, the magnitude of shear stress acting at the interface drastically increases and, thus, the failure of the film itself will facilitate the failure of interface. Therefore, the measured value of L_A does not represent the true adhesion force between the TiN film and the substrate because it is greatly affected by L_C. The decrease in L_A for the TiN films deposited above −100 V could be explained by the decrease in L_C which is due to the decrease in film hardness. The features of these cohesive and adhesive failures can be seen from the optical micrographs presented in Fig. 10(a) and (b) for the specimens deposited at the substrate bias of −75 and −200 V, respectively. In order to identify whether the TiN coating on the scratched track was detached from the martensitic stainless steel substrate, the areas of A and B on the specimen deposited at the substrate bias of −75 V were analyzed by WDS and its results are shown in Fig. 11. As can be seen in Fig. 11, the film elements, Ti and N, were

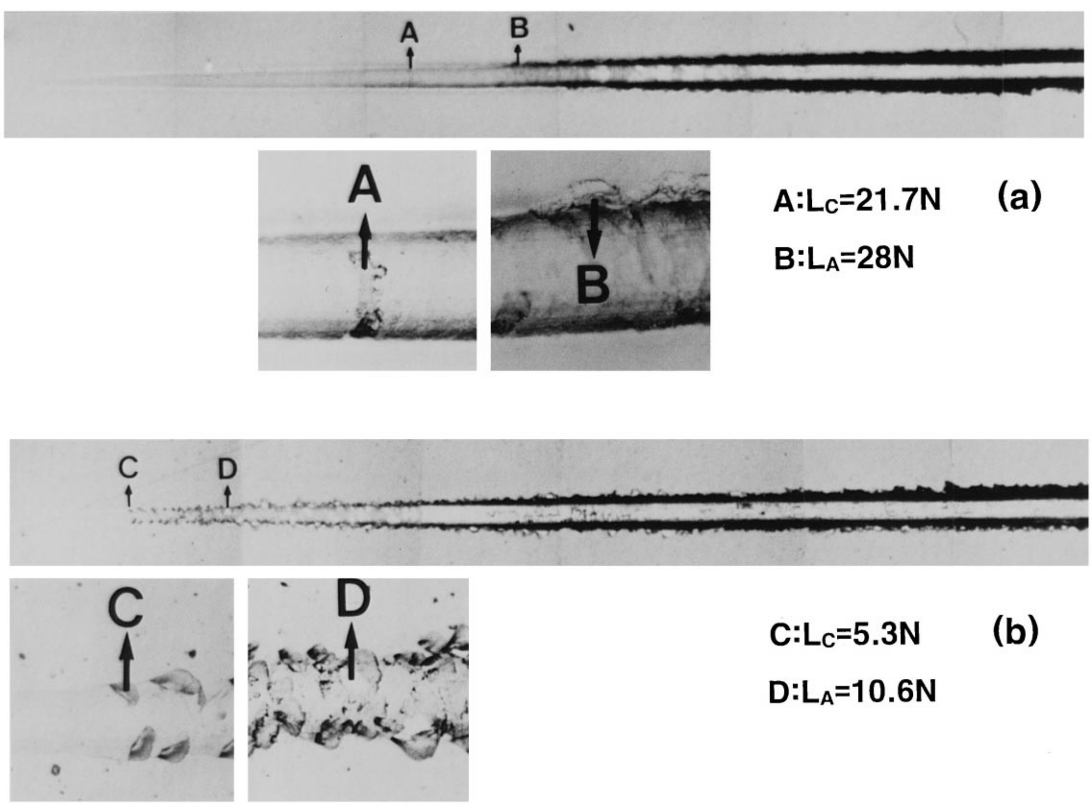

Fig. 10. Optical micrographs of ion plated TiN after the scratch adhesion test; (a) substrate bias = −75 V and (b) substrate bias = −200 V.

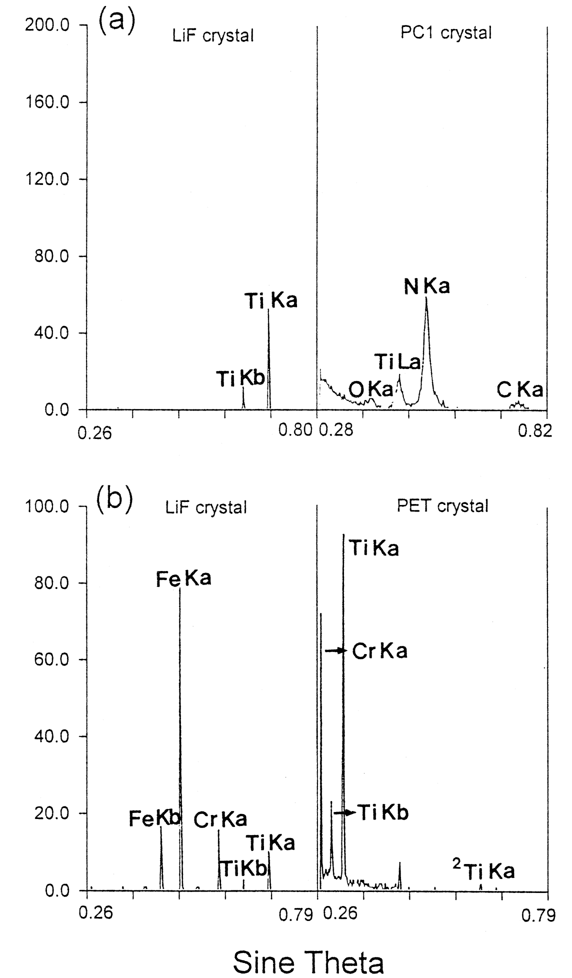

Fig. 11. WDS analysis of scratch adhesion tested trace of TiN film deposited at substrate bias = −75 V; (a) A area and (b) B area.

detected in area A and the substrate elements, Fe, Cr, etc., were detected in area B, which indicates the cohesive and the adhesive failure, respectively. The same results were obtained for the specimen deposited at the substrate bias of −200 V. The adhesion properties of the TiN films coated on Stellite 6B were almost similar to those on martensitic stainless steel.

3.4. Wear property of TiN film

Fig. 12 represents the wear track width and the frictional force measured as a function of substrate bias. The wear track width and the frictional force are in good agreement with each other. According to the wear test, the wear track width with the variation of substrate bias had a reciprocal relationship with the hardness. The wear track width of the TiN film deposited without the substrate bias was relatively large because of the low hardness but it decreased by the increase in hardness as the substrate bias increased. The specimen deposited at the bias of −75 V which had a maximum value of hardness showed the minimum values of the wear track width (0.18 mm) and the frictional force (3.3 N). The increase in wear track width for the TiN films deposited at above −100 V is thought to be due to the decrease in film hardness. Bull et al. [7] also reported that the wear resistance of TiN film increases with increasing the residual compressive stress up to the substrate bias of −120 V. At the same test conditions, the wear track widths of uncoated Stellite 6B and AISI 403 martensitic stainless steel were 0.42 and 1.68 mm, respectively, which were 2.3 and 9.3 times larger than that of TiN coated specimen at the bias condition of −75 V. Fig. 13 shows the tested surfaces of AISI 403 martensitic stainless steel (a), Stellite 6B (b) and TiN (−75 V) (c) observed by SEM. For the uncoated specimens, considerable roughenings and irregularities were observed on their worn surfaces. Particularly, severe plastic ploughing

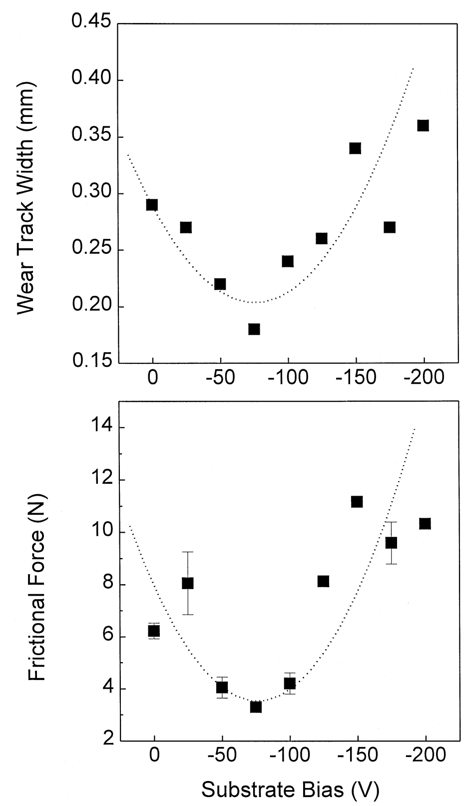

Fig. 12. Variation of wear track width and frictional force of TiN films with the substrate bias.

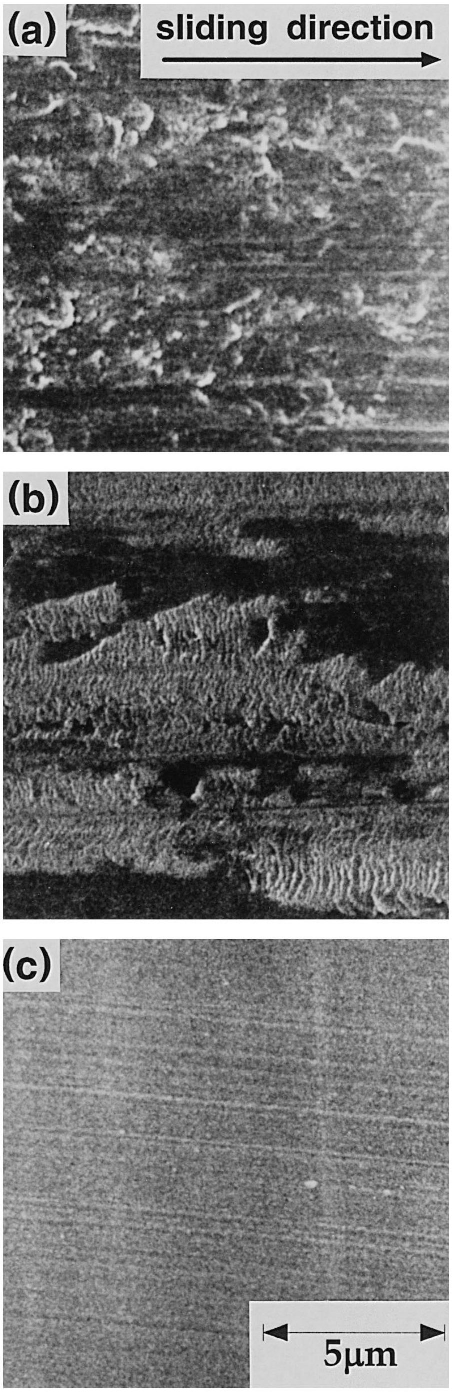

Fig. 13. Scanning electron micrographs of the worn surface; (a) AISI martensitic stainless steel, (b) Stellite 6B and (c) TiN (-75 V).

and spalling were seen in AISI 403 martensitic stainless steel, indicating that the severe wear was done. However, the specimen coated with TiN showed a finely scratched and relatively smooth surface. Consequently, the wear resistances of bare Stellite 6B and AISI 403 martensitic stainless steel were greatly improved by the coating of TiN film with appropriate substrate bias.

4. Conclusions

The increase of the substrate bias causes the increase of the residual compressive stress in TiN film and the preferential growth of TiN film with (111) plane. However, high biases (above -100 V) decrease the residual compressive stress due to the damage by too severe ion bombardment. The hardness of TiN film is proportional to the residual compressive stress and has a maximum value of 3400 kg/mm^2 at the bias voltage of about -75 V. The adhesion force of the biased specimen is improved compared with the unbiased one. The critical load for cohesive failure (L_C) shows a good correlation with the hardness. TiN coating by reactive magnetron sputter ion plating with appropriate substrate bias (about -75 V) greatly improves the wear resistances of martensitic stainless steel and Stellite.

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