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A Comparative Study on Microstructure and Tribological Properties of Si_3N_4 and TiN Thin Films Produced by IBED Method

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Abstract: In this paper, the tribological properties of Si_3N_4 and TiN thin films produced by ion beam enhanced deposition (IBED) method were compared on an SRV friction and wear testing machine. In order to understand the reasons of their excellent properties the microstructure, microhardness and bonding strength with the substrate were analysed by SEM, X-ray diffraction, Knoop hardness test and scratching test methods separately. The results show that the TiN(1) film exhibits the best tribological properties, which are closely related with its higher hardness and bonding strength.

1 INTRODUCTION

Materials with both high hardness and high toughness become more and more important for many industrial applications. Among them, the application of ceramic materials is developing steadily for internal combustion engines, machine tools, cutting tools and some others due to their high hardness, chemical stability and wear resistance. However, the considerably low toughness and difficult machinability restrict their development and a monolithic ceramic may not have the optimum surface characteristics for a specific tribological application. Therefore, the ceramic coating technique has special advantages, such as the possibility to select independently coating and base materials for a given application, the ability to maintain close dimensional tolerances of the coated workpiece, since very thin films are often sufficient, the good combination of strength and toughness provided by the base materials, the saving in costs and so on.

The ion beam enhanced deposition (IBED) is a newly developed vapour deposition technique. It can increase obviously the bonding strength of thin films with the substrate by the ion bombardment of the interface.[1] The ceramic films are synthesized by ion sputtering and ion mixing from different ion-sources, which can be controlled easily.

In this paper, the Si_3N_4 and TiN thin films were selected as coating materials on 52100 bearing steel, and their tribological properties were compared on the SRV testing machine in order to obtain a suitable ceramic film for its application in precision rolling bearings. The microstructure, microhardness and bonding strength with substrate of two films were also analysed for an understanding of their excellent tribological properties.

2 EXPERIMENTAL METHODS

2.1 Materials

The ball-on-disc contact model was adopted for friction and wear tests on an SRV testing machine. The Si_3N_4-and TiN thin films were deposited on the polished surface of disc specimens made from 52100 bearing steel with hardness of HRC60–62.

These films were also deposited on the single crystal silicon wafers for the SEM and X-ray diffraction analyses. The upper specimen was a hot pressed Si_3N_4 ball of 10 mm diameter with Knoop microhardness HK 2381.

2.2 Preparation of thin films

Two ion sources were used in the IBED apparatus as shown in Fig. 1. One source produced the argon ion beam for sputtering the silicon or titanium targets. Another source produced the nitrogen ion beam for reacting with silicon and titanium atoms and bombarding the interface. The parameters of deposition are shown in Table 1.

Before normal deposition, the cleaning bombardment by a nitrogen ion beam (20 KV and 10 mA) for 10 min and the interface ion-mixing for 10 min under the same conditions were used for each specimen.

The thickness of the films was about 1 μm.

2.3 Micro-analysis of thin films

The SEM was used to observe the morphology of the wear surface and the cross section of the thin films.

The X-ray diffraction method was adopted to identify their microstructures.

The micro-hardness of thin films was measured by a Knoop microhardness tester at a load of 5 g.

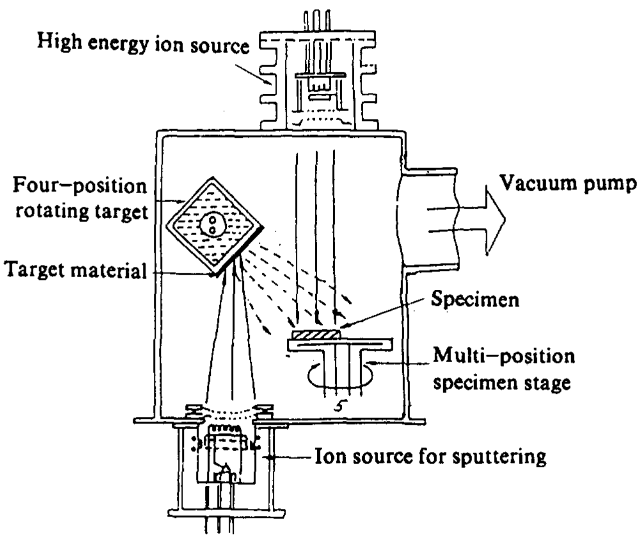

Fig. 1. Schematic of IBED apparatus.

The bonding strength of the thin films on the substrate was tested on a automatic scratching tester.

2.4 Friction and wear tests

On the SRV testing machine the friction and wear tests were all conducted with paraffin oil lubrication. The friction coefficient was recorded automatically, under constant conditions (amplitude 1 mm, time 30 min) with the variation of the load from 20 to 100N at a frequency of 15 Hz and with a variation in frequency from 15 to 55 Hz at a load 40N. The wear volume of the disc specimens under the same conditions was measured by a Taylor–Hobson profilometer.

3 RESULTS AND DISCUSSION

3.1 SEM analysis

Figure 2 shows the SEM morphology of the cross section of Si_3N_4 and TiN thin films deposited on the wafer under 10 000 × magnification. The thicknesses of them all are about 1 μm, but with different deposition time. This indicates that the deposition rate of TiN film is higher than that of Si_3N_4. From Fig. 2 it can also be deduced that the IBED films are quite compact, no columnar structure is revealed. Figure 3 shows the Si and Ti half-quantitative concentrations measured by EDX at the surface, interface and substrate corresponding to the positions of white spots on Fig. 2(b). The reduced concentration of Ti and occurrence of Si on the interface just demonstrate the effect of ion-mixing.

3.2 X-ray diffraction analysis

The results of X-ray diffraction analyses of thin films on 52100 steel are shown in Fig. 4. It can be deduced from these spectral curves that the microstructure of both Si_3N_4 and TiN films is mainly composed of microcrystals, and a certain amount of amorphous structure is also included, which is characterized by the widened peaks. Figure 4(a) indicates that the microstructure of Si_3N_4 film is β-Si_3N_4. Figure 4(b) and (c) tell us that only TiN (200) and TiN (220) were detected,

Table 1. Deposition parameters of IBED

Specimen number	Film	Nitrogen ions: Beam voltage (KV)	Nitrogen ions: Beam current (mA)	Argon ions: Beam voltage (KV)	Argon ions: Beam current (mA)	Deposition time (h)
1	Si_3N_4	4	7	3·60	130	6
2	TiN	4	6	3·60	130	4
3	TiN	15	3	3·60	130	4

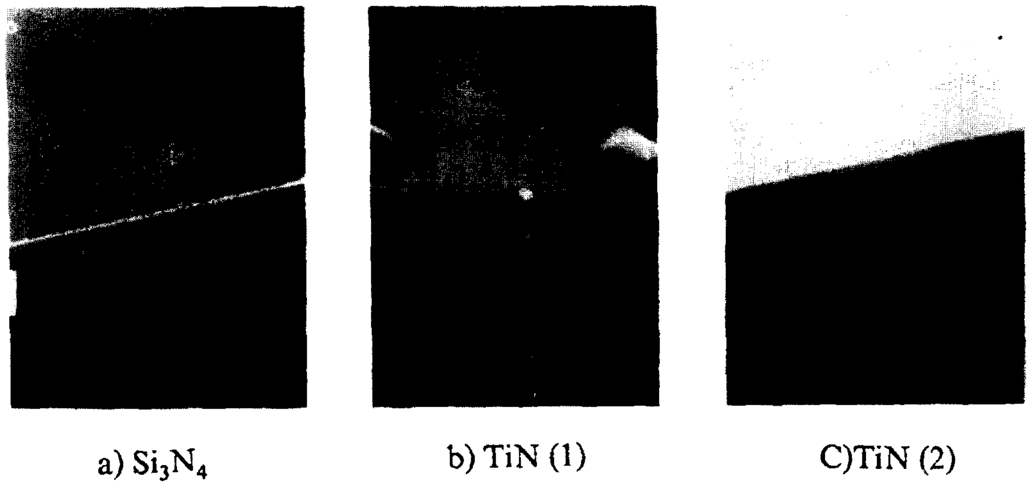

Fig. 2. Section views of IBED films under SEM.

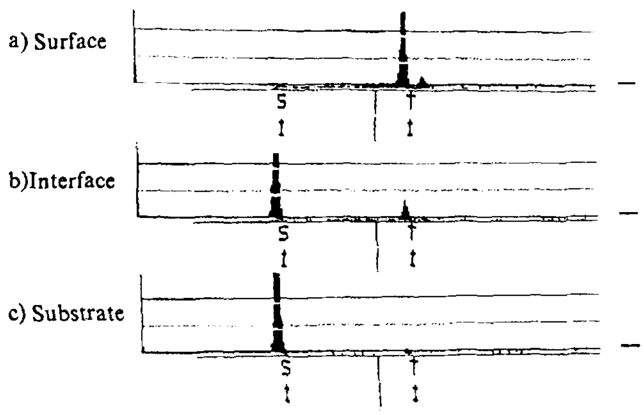

Fig. 3. Concentrations of Si and Ti at different positions on cross sections of TiN films by EDAX.

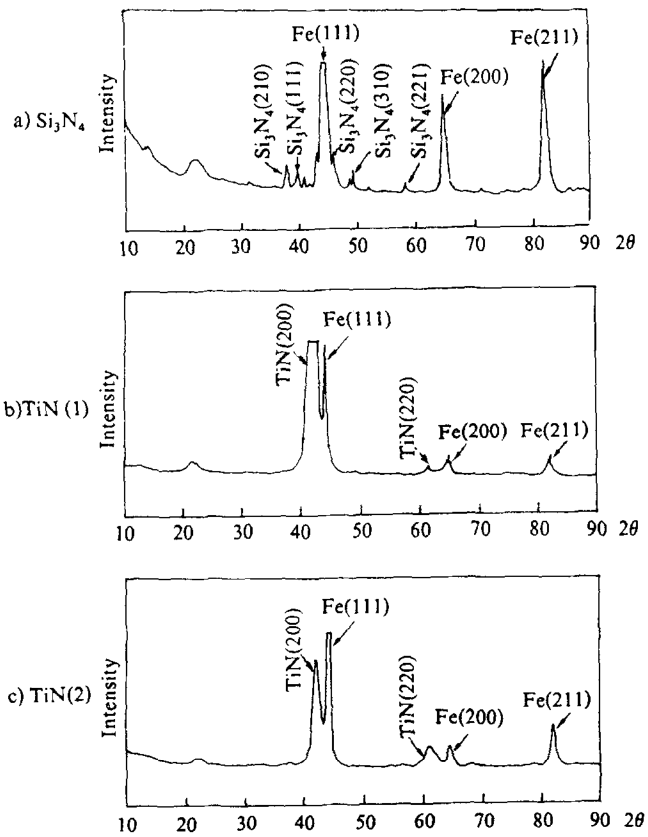

Fig. 4. Analysis results of X-ray diffraction for three IBED films on 52100 steel substrate.

another main peak TiN (111) did not appear. It indicates that a certain degree of texture of TiN crystals were formed in the films. At the same time, it can be found that the intensities of TiN (200) and TiN (220) have changed by comparing Fig. 4(b) with Fig. 4(c), i.e. the intensity of TiN (200) became lower and that of TiN (220) became larger when the nitrogen ion beam voltage changed from 4 to 15 kV. That means, the use of higher ion beam energy can restrict the growth of TiN crystals in a fixed direction and the development of texture.

3.3 Hardness and bonding strength measurements

The hardness of three IBED films was measured by a Knoop hardness tester under 5 g load. The results are shown in Table 2. It can be seen that the TiN films are harder than Si_3N_4, which coincides with the comparison of the hardness of bulk Si_3N_4 and TiN materials.[2] The hardness of TiN (1) films is obviously higher than that of TiN (2).

The difference in hardness for both TiN films is caused by different deposition parameters, which determine the different mechanisms in film formation.[3] In the case of the relatively low N^+ ion beam voltage and larger ion beam current the reaction mechanism is dominant. When the parameters are changed to a higher voltage and a lower current, the implantation mechanism will become dominant and a relatively lower nitrogen concentration than that of TiN (1) can be obtained because the lower current can offer only insufficient N^+, which must result in a decrease of its hardness.[4]

The results of bonding strength measurement are also shown in Table 2. It can be seen that the bonding strengths of all three IBED films are higher than 50N (the value generally reported in literature).[5] This indicates that the pre-cleaning of the substrate surface by high energy ion beam

Table 2. Hardness and bonding strength of IBED films on 52100 steel substrate

Films	Knoop hardness (p = 5 g)				Bonding strength (N)			
	1	2	3	Average	1	2	3	Average
Si_3N_4	2224·8	1970·7	1970·7	2054·6	53	55	46	51·3
TiN (1)	2531·3	2671·9	2465·2	2555·7	65	75	63	67·6
TiN (2)	2248·2	2465·5	2340·4	2351·3	63	58	53	58·0

bombardment and ion-mixing bombardment on the interface play a very important role for increasing the bonding strength on the substrate. The reason for the higher bonding strength of TiN compared to Si_3N_4 is probably due to the greater ion-mixing effect of the former (Fig. 3). The difference of bonding strength for TiN (1) and TiN (2) may be related to the different orientations of texture, which will result in a different lattice misfit and stress state on the interface.

3.4 *Tribological properties*

The tribological properties of three IBED films are shown in Figs 5–8. As a comparison those of 52100 bearing steel are also put in these figures. It can be found that:

(1) The friction coefficient of all specimens shows the obvious descending tendency with an increase in load (Figs 5 and 6). When the load reaches 100N, the friction coefficients almost approach the same level. This phenomenon can be explained by the gradual improvement of the surface roughness in the contact area during friction. The higher the load, the smoother the friction surface will be. Figure 6 shows the same tendency for the friction coefficient with an increase in frequency (sliding speed), but the tendency is much milder, and the friction coefficient even increases when the frequency is over 40 Hz. The explanation may be that the thickness of oil films is increased with an increase of sliding speed in the lower frequency range. When the frequency exceeds a certain value, the friction heat produced will reduce the viscosity and deteriorate the properties of the lubricating oil. As a

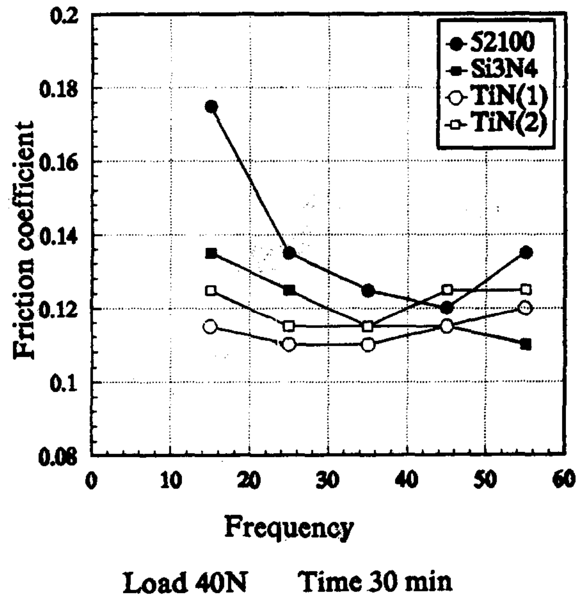

Fig. 6. The variation of friction coefficient with frequency.

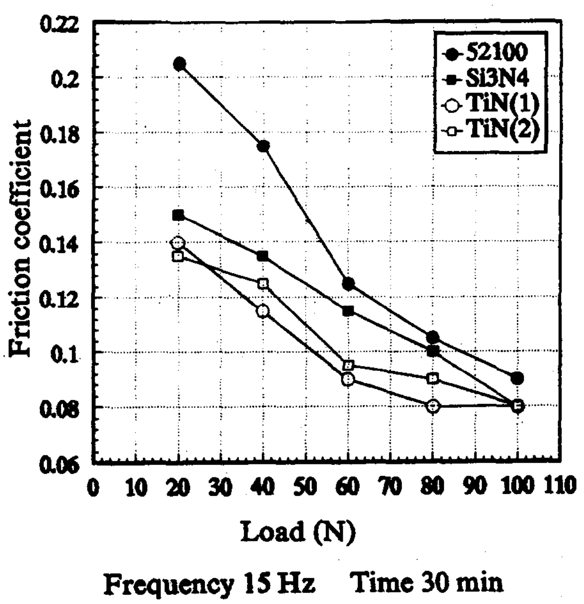

Fig. 5. The variation of friction coefficient with load.

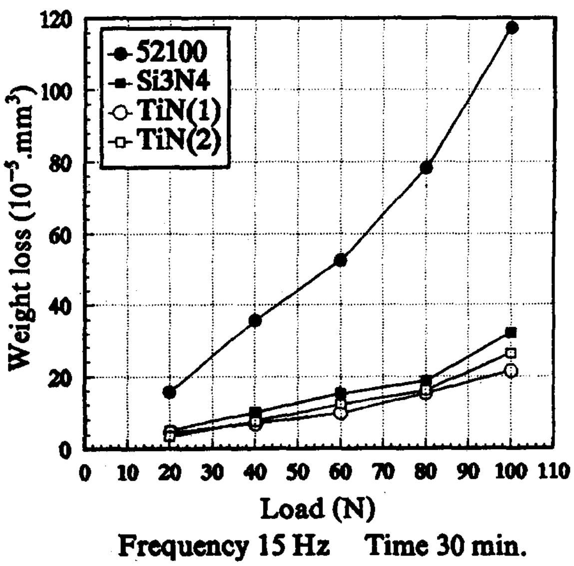

Fig. 7. The variation of weight loss with load.

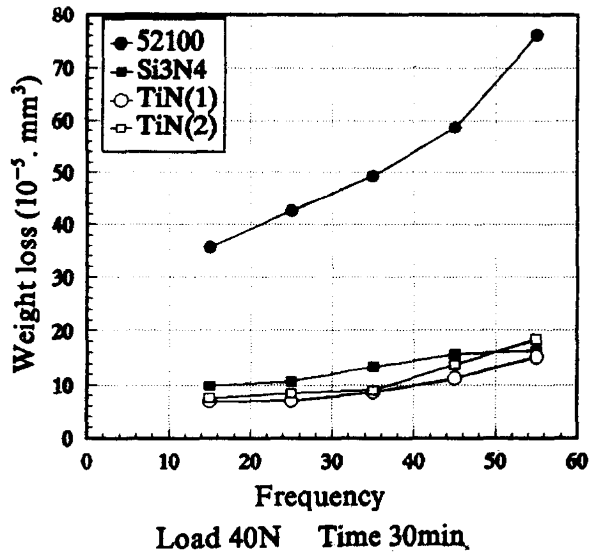

Fig. 8. The variation of weight loss with frequency.

consequence, the friction coefficient increases. Regarding friction temperature the effect of sliding speed is greater than that of load.[6]

(2) The friction coefficient of all IBED ceramic films is lower than that of 52100 steel, and the order of friction coefficient from high to low is as follows:

$$Si_3N_4 > TiN\ (2) > TiN(1)$$

The lower friction coefficient of ceramic films is obviously due to their much higher hardness than that of 52100 steel which is easily deformed plastically during friction. The friction coefficient of Si_3N_4 is higher than that of TiN; this can be explained by the point of view that both the ball and disc were made from the same material, which always results in a greater affinity than the pair of different materials. As for the difference in friction coefficient of TiN (1) and TiN (2), the higher hardness and degree of texture of TiN (1) probably play an important role.

(3) All the IBED films show much better wear-resistance than 52100 steel, especially in the higher load and frequency ranges. The weight loss of 52100 steel increases more with an increase in load and frequency, compared to IBED films. The wear-resistance of three IBED films doesn't show a large difference, the TiN (1) is the most wear-resistant one.

All these phenomena are obviously related to the higher hardness and greater bonding strength of the IBED films.

Finally the wear tracks of these films were observed under SEM. Their wear morphologies are shown in Figs 9 and 10. It can be found that the dominant wear mechanism is abrasive wear, the only difference between Si_3N_4 and TiN is reflected by the surface roughness, the latter shows more shallow microcutting or ploughing depth due to its higher hardness.

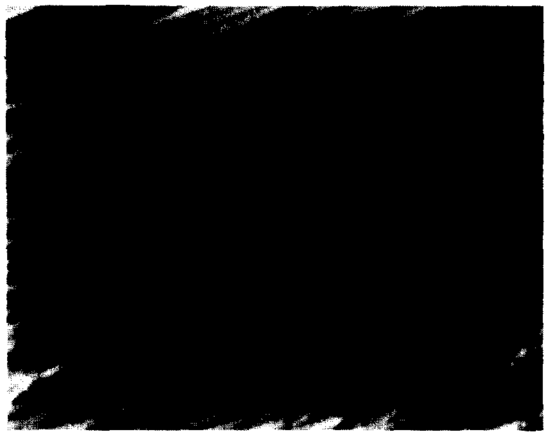

Fig. 9. SEM morphology of wear track on Si_3N_4 film, × 1000.

Fig. 10. SEM morphology of wear track on TiN film, × 1000.

4 CONCLUSIONS

(1) The microstructures of IBED Si_3N_4 and TiN films are composed mainly of microcrystals, there is also a certain amount of amorphous structure included. A certain degree of texture was detected by X-ray diffraction in the TiN films, it became less developed when the deposition parameters were changed to higher voltage and lower current of the N^+ ion beam.

(2) Among three IBED films the TiN (1) shows the highest hardness and bonding strength on the 52100 steel substrate. It seems that the effect of ion-mixings is more prominent for the TiN film.

(3) All the IBED ceramic films show a much lower friction coefficient than 52100 steel and an excellent wear-resistance. The order of their tribological properties from low to high is as follows:

$$Si_3N_4 \rightarrow TiN\ (2) \rightarrow TiN(1)$$

which is determined by their hardness and bonding strength with the substrate.

(4) The dominant wear mechanism of IBED films is abrasive wear.

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