Improved Mechanical Properties of Al$_2$O$_3$ Ceramics by Sputtered TiN Coatings

Chia-Hui Chien$^1$, Feng-Min Lai$^2$, Chih-Wen Cheng$^1$, Sin-Liang Ou$^{2,*}$, Shu-Chuan Liao$^3$, Tsan-Ming Su$^3$ and Yao-Tsung Yang$^3$

$^1$Dentistry, Chi-Mei Medical Center, Yongkang Dist., Tainan 71004, Taiwan, R.O.C.
$^2$Department of Materials Science and Engineering, Da-Yeh University, Changhua 51591, Taiwan, R.O.C.
$^3$Bachelor Program for Design and Materials for Medical Equipment and Devices, Da-Yeh University, Changhua 51591, Taiwan, R.O.C.

In this study, TiN thin films have been prepared as the coating layers on Al$_2$O$_3$ ceramic substrates to enhance the mechanical properties of Al$_2$O$_3$ ceramics. TiN films with various thicknesses of 0.5 and 1 µm were deposited by DC sputtering at room temperature. The TiN film prepared on the Al$_2$O$_3$ substrate has a columnar structure without large bumps or steps formed on the film's surface. Without the TiN coating, the average friction coefficient of the Al$_2$O$_3$ substrate was 0.51. As 0.5- and 1-µm-thick TiN films were coated on Al$_2$O$_3$ substrates, the average friction coefficients of these two samples reduced to 0.36 and 0.32, respectively, revealing the tribological characteristics of Al$_2$O$_3$ ceramic enhanced with the TiN coating. Additionally, the 1-µm-thick TiN/Al$_2$O$_3$ sample possesses a slightly higher attrition resistance than that of the 0.5-µm-thick TiN/Al$_2$O$_3$ sample, and this can be also confirmed by performing the elemental mapping method on the wear-treated samples. From the adhesion performances, we observed no critical load of L$_{C1}$ appeared in these two samples during the scratch test, while the critical load of L$_{C2}$ values were 11 and 9 N for 0.5-µm-thick TiN/Al$_2$O$_3$ and 1-µm-thick TiN/Al$_2$O$_3$, respectively. Due to the increment of TiN thickness, the internal stress formed in the film would increase. This is the reason why the 1-µm-thick TiN/Al$_2$O$_3$ sample has a lower critical load of L$_{C1}$. Obviously, the 0.5-µm-thick TiN film coated on the Al$_2$O$_3$ substrate has a better adhesion characteristic. According to these results, the sputtered TiN coating is indeed useful for improving the mechanical properties of Al$_2$O$_3$ ceramics, in particular for the 0.5-µm-thick TiN coating. [doi:10.2320/matertrans.M2017097]

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1. Introduction

In recent years, many ceramic materials have been proposed to apply for mechanical, biomedical, optoelectronic, semiconductor and aerospace applications. Among these ceramic materials, alumina (aluminum oxide, Al$_2$O$_3$) is widely used in different technical applications because of its excellent characteristics. It has the same crystal structure as sapphire material. Since the alumina possesses high electrical insulation, it is used in electrical components for decades. Additionally, owing to its high strength, corrosion resistance and wear resistance, the alumina is also applied for many mechanical parts. However, for some specific applications, the strength and wear resistance are not high enough and still need to be improved. Especially for the medical applications (for example, the denture applications), if the mechanical properties of alumina materials are not high enough, it will lead to the diseases and life-threatening illness to human. As mentioned above, how to further enhance the mechanical properties of alumina materials is a very important issue.

For the sake of improving the mechanical properties of materials, the surface coatings are often used. In various coating materials, TiN thin films are the most popular coatings for commercial applications$^{1-3}$. Actually, TiN coatings are commonly used for the machining tools to enhance their working efficiency and lifetime performance. The TiN films are coated on the samples for high wear applications, and they are regularly subject to cyclic loading during the machining process. On the other hand, the TiN films can be prepared by several methods such as physical vapor deposition (PVD)$^{4-6}$ and chemical vapor deposition (CVD)$^{7-9}$. Among the PVD techniques, sputtering is quite suitable for the TiN growth since the deposited films have several advantages including high film density, high uniformity in thickness, smooth surface and good adhesion$^{10-12}$.

Up to present, although several materials are presented for the coating on the Al$_2$O$_3$ ceramics to improve their mechanical properties, there is seldom research about the TiN coating on the Al$_2$O$_3$ ceramic. In this study, TiN thin films were deposited on the surfaces of Al$_2$O$_3$ ceramics by sputtering to enhance the mechanical properties. The TiN films with various thicknesses of 0.5 and 1 µm were prepared. Moreover, the Al$_2$O$_3$ substrate without the TiN coating was also prepared as a contrasted sample. Mechanical properties of these samples were characterized using friction, wear and scratch tests.

2. Experimental Procedure

In our work, the ceramic materials used for the TiN deposition were Al$_2$O$_3$ substrates (99.5% purity Al$_2$O$_3$). The density, rupture strength and compressive strength of the Al$_2$O$_3$ substrate are 3.9 ± 0.03 g/cm$^3$, 294.2 MPa and 2500–3400 MPa, respectively. Additionally, the hardness of this substrate is HRa89. The area of the Al$_2$O$_3$ substrate is 12.7 × 12.7 mm$^2$, while its height is 2 mm. Before the TiN coating process, the Al$_2$O$_3$ substrates were polished with the sand paper and then ultrasonically cleaned in ethanol for 10 min to remove organics and other impurities. After polishing, the surface roughness (root-mean-square roughness using a 25 µm$^2$ scan area) of the Al$_2$O$_3$ substrates was approximately 0.3 µm. In this study, to improve the mechanical properties of Al$_2$O$_3$, the TiN film was coated on the Al$_2$O$_3$ substrate.
The TiN films with two thicknesses of 0.5 and 1 μm were prepared at room temperature by DC sputtering. A stoichiometric ceramic TiN target (99.99% purity) with 7.62 cm diameter was used for the TiN coating. The distance between the TiN target and Al_{2}O_{3} substrate was kept at 5 cm. The sputtering power of TiN target was fixed at 800 W. When the base pressure of the sputtering chamber reached to 6.67 × 10^{-5} Pa, pure N_{2} gas (99.9999%) was introduced into the chamber, and the working pressure was maintained at 101.325 kPa. For the growths of 0.5- and 1-μm-thick TiN films, the deposition time should be increased to 4 and 8 hours, respectively. Based on the compositional analyses, these sputtered TiN films have a constant stoichiometric ratio of Ti:N approximately 1.

The growth rate and thickness of TiN film were measured by an α-step profilometer. Surface morphologies of samples can be demonstrated by scanning electron microscopy (SEM). The element distributions on the sample surface were characterized using SEM elemental mapping technique. The compositional analyses of samples were determined by energy dispersive x-ray spectroscopy (EDS). Mechanical properties of samples were conducted to various experiments such as tribological (friction and wear) and scratch tests. Friction and wear tests both were carried out on a pin-on-disk machine. In this equipment, the tungsten carbide (WC) ball with a diameter of 10 mm was served as the pin. The samples were tested against WC balls at room temperature. In these pin-on-disk tests, normal load, linear sliding speed, sliding distance and relative humidity were kept at 2 N, 2 cm/s, 200 m and 50%, respectively. Through the experiments, the relationship between the friction coefficients of these samples increased. This could be attributed to the formation of wear debris generated from the crack on the friction surface. Thus, according to the results of friction tests, it can be presumed that the dominant wear mechanism of these three samples is adhesive wear because of the behavior of the wear debris. Although the

![Fig. 1](image)

Fig. 1 (a) Plan-view and (b) cross-sectional SEM images of the 0.5-μm-thick TiN film deposited on Al_{2}O_{3} substrate. (c) Cross-sectional SEM image of the 1-μm-thick TiN film deposited on Al_{2}O_{3} substrate.

3. Results and Discussions

The morphologies of the TiN films deposited on the Al_{2}O_{3} substrates were observed by SEM, as shown in Fig. 1. Figure 1(a) shows the plan-view SEM image of the 0.5-μm-thick TiN/Al_{2}O_{3} sample. It is obvious that there are many grains with the finite size uniformly distributed on the sample surface. Figure 1(b) displays the SEM image of the cross section of the 0.5-μm-thick TiN/Al_{2}O_{3} sample. We can observe that there are no large bumps or steps formed on the surface of the TiN film. In addition, the TiN film possesses a columnar structure, and its thickness is indeed approximately 0.5 μm. It can be also found that the TiN coating is homogeneous, dense, uniform and compact. Actually, the coating films deposited by sputtering usually have a columnar structure without the formation of macroparticles. Besides, the cross-sectional SEM image of the 1-μm-thick TiN film on the Al_{2}O_{3} substrate is shown in Fig. 1(c). The morphological feature of the 1-μm-thick TiN is quite similar to that of the 0.5-μm-thick TiN.

The friction tests were performed on the Al_{2}O_{3} substrate, 0.5-μm-thick TiN/Al_{2}O_{3} substrate and 1-μm-thick TiN/Al_{2}O_{3} substrate. In these measurements, the sliding distance was increased from 0 to 200 m. Figure 2 shows the friction coefficients as a function of sliding distance for these three samples. We can observe that these three samples all possessed a similar friction coefficient at the beginning of the measurements. When the sliding distance was increased, the friction coefficients of these samples increased. This could be attributed to the formation of wear debris generated from the crack on the friction surface. Thus, according to the results of friction tests, it can be presumed that the dominant wear mechanism of these three samples is adhesive wear because of the behavior of the wear debris.
friction coefficients of these three samples all increased with increasing the sliding distance, the difference between their increment rates was obvious. When the sliding distance was raised from 0 to 200 m, the friction coefficient of the Al$_2$O$_3$ substrate increased from 0.15 to 0.64. This indicates that the attrition resistance of the Al$_2$O$_3$ substrate would become apparently poor as the sliding distance is enlarged to a certain range. Meanwhile, for 0.5-μm-thick TiN/Al$_2$O$_3$ and 1-μm-thick TiN/Al$_2$O$_3$ samples, the friction coefficients increased from 0.15 to 0.5 and from 0.1 to 0.37, respectively. It is obvious that the deposition of TiN film is helpful to improve the tribological characteristics of the sample. Besides, it also can be found that the thicker the TiN film is, the lower the friction coefficient of the sample is. Based on the recorded friction coefficients with increasing the sliding distance (Fig. 2), the average friction coefficients of these three samples can be calculated, as shown in Fig. 3. For the Al$_2$O$_3$ substrate, 0.5-μm-thick TiN/Al$_2$O$_3$ and 1-μm-thick TiN/Al$_2$O$_3$ samples, the average friction coefficients are determined to be 0.51, 0.36 and 0.32, respectively. The relatively higher friction coefficient shown in the sample coated with the thinner TiN could be due to the substrate influence. In other words, for the sample with the thinner coating, the friction coefficient might be affected by the roughness of substrate surface owing to the penetration of asperities, resulting in its higher friction coefficient$^{14}$. According to the tribological properties, it seems that the deposition of TiN film with the thickness of 1 μm on the substrate is more feasible for enhancing the mechanical properties of Al$_2$O$_3$.

Then, the wear tests for these three samples were carried out and observed by SEM. After performing the pin-on-disk wear tests, the plan-view SEM images of the Al$_2$O$_3$ substrate, 0.5-μm-thick TiN/Al$_2$O$_3$ substrate and 1-μm-thick TiN/Al$_2$O$_3$ substrate are displayed in Figs. 4(a), (b) and (c), respectively. In Fig. 4, the wear tests were performed on the middle regions of these three SEM images, as marked by the red dotted lines. Without the deposition of TiN film, the surface of Al$_2$O$_3$ substrate was much easily peeled off after the wear test, as shown in Fig. 4(a). On the other hand, due to the coating of TiN film, the wear resistance of Al$_2$O$_3$ substrate can be improved efficiently. As shown in Figs. 4(b) and (c), it was found that there was almost no peeling problem on the surfaces of Al$_2$O$_3$ substrates of these two samples (0.5-μm-thick TiN/Al$_2$O$_3$ substrate and 1-μm-thick TiN/Al$_2$O$_3$ substrate). This reveals the TiN film can indeed act an important role against the wear. However, the difference between the wear-treated surfaces after coating 0.5- and 1-μm-thick TiN films on Al$_2$O$_3$ substrates is not obvious. Thus, the SEM-EDS measurements were performed on these two samples subsequently.

To further identify the elemental distributions of samples after the wear tests, the SEM elemental mapping technique was used. Figure 5 displays the surface morphologies observed by SEM and the mappings of the elements for the wear-treated 0.5-μm-thick TiN/Al$_2$O$_3$ and 1-μm-thick TiN/Al$_2$O$_3$ samples. The samples were predominantly composed of N, O, Al and Ti elements, and these four elements were indexed by red, green, blue and gray colors, respectively. In general, the brighter the distribution map is, the larger the elemental concentration is. The differences in the N, O and Ti distribution maps between these two samples are difficult to distinguish. Nevertheless, the brightness of Al distribution map of the 0.5-μm-thick TiN/Al$_2$O$_3$ is obviously higher than that of the 1-μm-thick TiN/Al$_2$O$_3$. Apparently, after the wear treatment, the 1-μm-thick TiN/Al$_2$O$_3$ sample possessed less Al concentration on its surface, resulting from the deposition of the thicker TiN film. Further elemental analyses for the surfaces of these two wear-treated samples are carried out using the EDS measurements, as shown in Table 1. The N, O, Al and Ti concentrations for the 0.5-μm-thick TiN/Al$_2$O$_3$ sample are measured to be 11.74, 33.86, 13.65 and 40.75 mass%, respectively. Meanwhile, these four concentrations for the 1-μm-thick TiN/Al$_2$O$_3$ sample are 17.02, 32.43, 45.8 and 44.57 mass%, respectively. As observed in Fig. 5, the Al concentration of the wear-treated 1-μm-thick TiN/Al$_2$O$_3$ sample was much less than that of the 0.5-μm-thick TiN/Al$_2$O$_3$ sample. In the meantime, the Ti concentration of the wear-treated 1-μm-thick TiN/Al$_2$O$_3$ sample was slightly more than that of the 0.5-μm-thick TiN/Al$_2$O$_3$ sample. The difference in the Ti concentration between these two samples was only 5.22 mass%. Based on the results, the
1-μm-thick TiN/Al2O3 sample has a higher attrition resistance in comparison to the 0.5-μm-thick TiN/Al2O3 sample. Finally, the adhesion performances of the TiN-coated Al2O3 samples were also analyzed via the scratch tests. Figures 6 and 7 show the observations of scratch tracks by optical microscopy (OM) and the acoustic emission signals detected during the scratch tests for 0.5-μm-thick TiN/Al2O3 and 1-μm-thick TiN/Al2O3 samples, respectively. Here, it should be mentioned that the failure values of the sample can be determined by the critical loads of LC1 and LC2. The first critical load of LC1 is related to the onset of tensile cracks, which indicates the non-continuous small adhesion rupture (cohesive failure) in the coated film. Moreover, the second load of LC2 is representative of the onset of chipping failure or the continuity of large spallation, which reveals the adhesive failure between the coated film and the substrate. According to our observations, the complete removal of coated TiN films didn’t occur in 0.5-μm-thick TiN/Al2O3 or 1-μm-thick TiN/Al2O3 samples. This suggests that there is no critical load of LC2 found in these two samples during the scratch test. Additionally, for 0.5-μm-thick TiN/Al2O3 and 1-μm-thick TiN/Al2O3 samples, their critical load values of LC1 were measured to be 11 and 9 N, respectively. The lower critical load of LC1 appeared in the 1-μm-thick TiN/Al2O3 sample could be attributed to an increment of the internal stress, resulting from its thicker TiN coating. In view of the above, although the attrition resistance of the TiN-coated sample can be improved by increasing the coating thickness, the consequential degradation in the adhesion performance between the 1-μm-thick TiN film and the Al2O3 substrate will reduce its practical feasibility. On the other hand, in spite of the fact that the attrition resistance of the 0.5-μm-thick TiN/Al2O3 sample is slightly lower than that of the 1-μm-thick TiN/Al2O3 sample, the adhesion characteristics present that the TiN film with a thickness of 0.5 μm can be more suitable as a coating layer on the Al2O3 substrate. In this research, it confirms that the 0.5-μm-thick TiN/Al2O3 sample has high potential for enhancing the mechanical characteristics of Al2O3 ceramics. In the future, the TiN coating technique on the Al2O3 ceramics will further be used for denture applications.

### 4. Conclusion

The sputtered TiN thin films with various thicknesses of 0.5 and 1 μm were coated on Al2O3 ceramic substrates to enhance their mechanical properties. The columnar structure was formed in the TiN film without any large bumps or steps on the surface. The average friction coefficients with a sliding distance from 0 to 200 m for the Al2O3 substrate, 0.5-μm-thick TiN/Al2O3 and 1-μm-thick TiN/Al2O3 samples are 0.51, 0.36 and 0.32, respectively. It is apparent that there is an improvement in the attrition resistance of the Al2O3 sample after depositing the TiN film. Additionally, the attrition resistance of the sample is enhanced with increasing the thickness of TiN coating. However, when the TiN coating was used for the Al2O3 ceramic, both tribological and adhesion properties should be considered. During the
scratch test, 0.5- and 1-μm-thick TiN films were not removed, indicating no critical load of \( L_{C2} \) generated in these two TiN/Al\(_2\)O\(_3\) samples. Meanwhile, the critical load of \( L_{C1} \) values of 11 and 9 N can be evaluated in 0.5-μm-thick TiN/Al\(_2\)O\(_3\) and 1-μm-thick TiN/Al\(_2\)O\(_3\) samples, respectively. Because the film’s internal stress increased with increasing its thickness, the 1-μm-thick TiN/Al\(_2\)O\(_3\) sample possessed the lower critical load of \( L_{C1} \) and a worse adhesion performance. Based on the results, the TiN films prepared by sputtering can successfully play the role as the coating layers on the Al\(_2\)O\(_3\) ceramics to enhance their mechanical characteristics, especially for the TiN film with a thickness of 0.5 μm.

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