Journal of the European Ceramic Society 22 (2002) 2869–2876

www.elsevier.com/locate/jeurceramsoc

Characterization and tribological investigation of sol-gel Al_2O_3 and doped Al_2O_3 films

Wenguang Zhang[a,b,*], Weimin Liu[b], Chengtao Wang[a]

[a]Institute of Life Quality via Mechanical Engineering, School of Mechanical and Engineering, Shanghai Jiao Tong University, Shanghai 200030, PR China

[b]State Key Laboratory of Solid lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

Received 4 October 2001; received in revised form 13 March 2002; accepted 24 March 2002

Abstract

Thin films of Al_2O_3 and doped Al_2O_3 were prepared on a glass substrate by dip coating process from specially formulated ethanol sols. The morphologies of the unworn and worn surfaces of the films were observed with atomic force microscope (AFM) and scanning electron microscope (SEM). The chemical compositions of the obtained films were characterized by means of X-ray photoelectron spectroscopy (XPS). The tribological properties of obtained thin films sliding against Si_3N_4 ball were evaluated and compared with glass slide on a one-way reciprocating friction tester. XPS results confirm that the target films were obtained successfully. The doped elements distribute in the film evenly and exist in different kinds of forms, such as oxide and silicate. AFM results show that the addition of the doped elements changes the structure of the Al_2O_3 films, i.e., a rougher and smoother surface is obtained. The wear mechanisms of the films are discussed based on SEM observation of the worn surface morphologies. As the results, the doped films exhibit better tribological properties due to the improved toughness. Sever brittle fracture is avoided in the doped films. The wear of glass is characteristic of brittle fracture and severe abrasion. The wear of Al_2O_3 is characteristic of brittle fracture and delamination. And the wear of doped Al_2O_3 is characteristic of micro-fracture, deformation and slight abrasive wear. The introduction of ZnO is recommended to improve the tribological property of Al_2O_3 film.

Keywords: Al_2O_3; Dopants; Films; Sol-gel process; Tribological properties

1. Introduction

Sol-gel process has many advantages, such as easy composition control and fabrication of large area thin films, film homogeneity, low cost, and a simple fabrication cycle. Therefore, it could be practical to make use of sol-gel technique to prepare thin films of desired tribological properties.[1] Over the last decades, sol-gel thin films have found wide applications in optical, microelectronics, photo-electronics industries.[1] Meanwhile, they are also applied for purpose of protection from scratching and corrosion.[1] ZrO_2 and hybrid inorganic-organic thin films have been prepared by sol-gel process for protection of aluminum and glass substrates.[2,3] The physical and mechanical properties of the films as protective materials have been increasingly focused on.[4,5] However, less knowledge is available about their tribological properties. This is also true for sol-gel Al_2O_3 based film materials, though extensive investigations have been concerned with their performance as an optical, microelectronic or mechanical material. Liu and co-workers investigated the tribological properties of TiO_2[6] and Al_2O_3 films[7] in detail. They found that the tribological properties of these sol-gel oxide films are closely related to their composition and structure.

Doping is widely applied to improve the mechanical or tribological properties of thin hard films.[8] Different methods, such as d.c. or r.f. plasma-assisted chemical vapor deposition (PACVD), sputtering, and ion beam deposition etc., have been applied to prepare doped films.[8,9] It is also feasible to use the sol-gel method for such processing.[10,13] Many investigations have been focused on the functional properties of the doped

* Corresponding author. Fax: +86-21-5258-1413.
E-mail address: zwg73@163.net (W. Zhang).

0955-2219/02/$ - see front matter
PII: S0955-2219(02)00063-8

films.[10–12] Nevertheless, only a few are concerned with the mechanical properties of doped film.[13] The influence of the doped elements on the tribological properties of the sol-gel film is not well understood.[9,14] The need of correlating between film processing, coating properties, and their tribological behavior becomes more pressing.[15] In this paper, Al_2O_3, Cu and Cu, Zn doped Al_2O_3 films (coded as D, D1, and D2 respectively) are prepared by sol-gel method. The as-prepared films were characterized by means of XPS and AFM. The worn surfaces of the films were observed with SEM. The tribological properties of the films were investigated with emphasis on revealing the relation between the tribological properties and the composition and structure of the films.

2. Experimental

2.1. Sample preparation

For the preparation of the ethanol sol, crystal aluminum chloride (99.99%), ammonia, glacial acetic acid, acetylacetone (AcAc), copper nitrate, and crystal zinc acetate were commercially obtained and used without further purification. Excess ammonia solution (5M) was added dropwise at room temperature to an aqueous aluminum chloride solution (0.13 M) of 100 ml. The final *p*H of the solution was 9. The hydrated precipitate so formed was filtered off, washed three times with pure water and ethanol respectively, aged for 2 days, and then peptized with glacial acetic acid in ethanol (room temperature for 1 h under stirring) to obtain 100 ml translucent, homogeneous, and stable sol (D). Subsequently, 1 ml AcAc was added. The final *p*H of the solution was about 4. Sol of Cu doped Al_2O_3 film (D1) is prepared by adding 0.004 mol (1 g) $Cu(NO_3)_2{\bullet}5H_2O$ to 100 ml solution D under stirring, while that of Cu, Zn doped Al_2O_3 film (D2) is obtained by adding 0.0045 mol (1 g) $Zn(CH_3COO)_2{\bullet}2H_2O$ to 100 ml solution D1 under stirring, which aged for 24 h for film preparation.

The films were coated on glass substrate by the dip coating process, at a substrate drawing speed of 38 cm/min, dried at room temperature for 15 min, and finally fired at 500 °C for 20 min, followed by cooling to the ambient atmosphere in the oven. The glass substrate was cleaned with ethanol-potassium hydroxide solution in an ultrasonic bath for 20 min, washed with distilled water and then dried in an atmospheric oven before used.

2.2. Experimental apparatus and measurements

XPS analysis was conducted on a XPS/AES (Model PHI-5702) system by using Mg-K_α radiation operating at 250 W and a pass energy of 29.35 eV. The binding energy of C1s (284.6 eV) was used as the reference. The depth profiling XPS was performed with Ar^+ ion gun bombardment. The surface morphology of the prepared thin films was observed with an atomic force microscope (AFM) (Model SPM-9500) and the corresponding friction force illustrated by voltage indirectly. The higher the voltage, the higher the friction force will be. The worn surfaces of the films were characterized with a scanning electron microscope (SEM) (Model JSM-5600LV).

Table 1
Physical and mechanical properties of Si_3N_4 ball

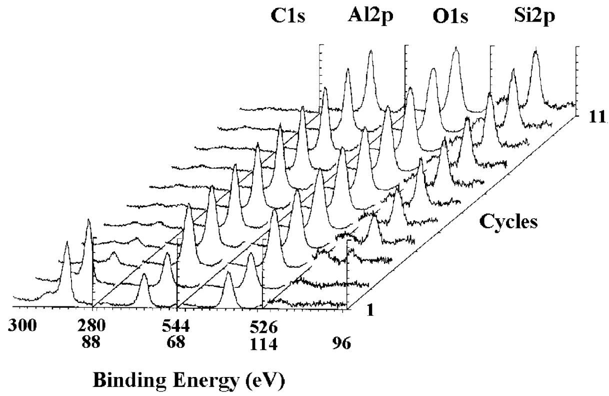
Relative density (%)	Hardness HRA	Fracture toughness (MPa m$^{1/2}$)	Fracture strength (MPa)
99	>90	6–9	500–700

The tribological properties of the films sliding against a fixed Si_3N_4 or SAE52100 ball (diameter 3 mm) were evaluated on a one-way reciprocating friction tester (Kyowa DF·PM Model) at a sliding velocity of 90 mm min^{-1} and a sliding distance 7 mm for each pass, at a normal force 3 and 0.5 N in ambient conditions (relative humidity: 40~44%). The physical and mechanical properties of the tested Si_3N_4 ball are shown in Table 1. The coefficient of friction and sliding passes were recorded automatically. In the whole sliding process the friction coefficient keeps stable with very little fluctuation for a short or long period and then rises to a higher stable value at last several or dozen of passes, the corresponding sliding pass numbers are recorded as the wear life of the film. Three replicate tests were carried out for each specimen and the average friction coefficients and wear lives of the three replicate tests were cited in this article. The relative error for the replicate tests was no more than 5%. Prior to the friction and wear test, all the samples were cleaned in an ultrasonic bath with ethanol and acetone for 10 min and then dried in hot air.

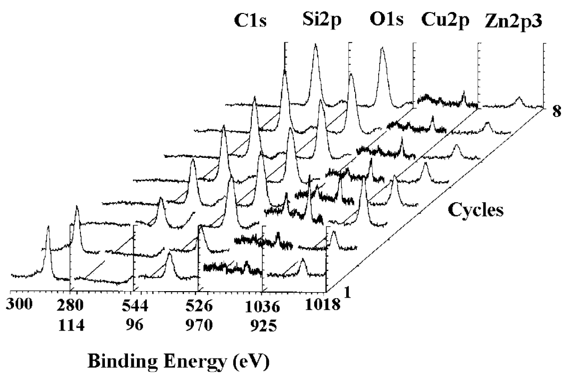
3. Results and discussion

3.1. Characterization of the film

Fig. 1(a) shows the XPS depth profiles of film D. It can be seen on the very out surface of D the binding energy of Al_{2p} at 74.30eV is consistent with that of sapphire Al_2O_3,[16] indicating the target Al_2O_3 film has been successfully obtained. The signal of Si_{2p} is too weak to be detected, implying that the very out surface of D is covered by pure Al_2O_3 film. After three cycles of sputtering the peak of Si_{2p} at 103.6 eV is possibly due to SiO_2.[16] The peak of C_{1s} exists even after five



(a) XPS profile of D



(b) XPS profile of D2

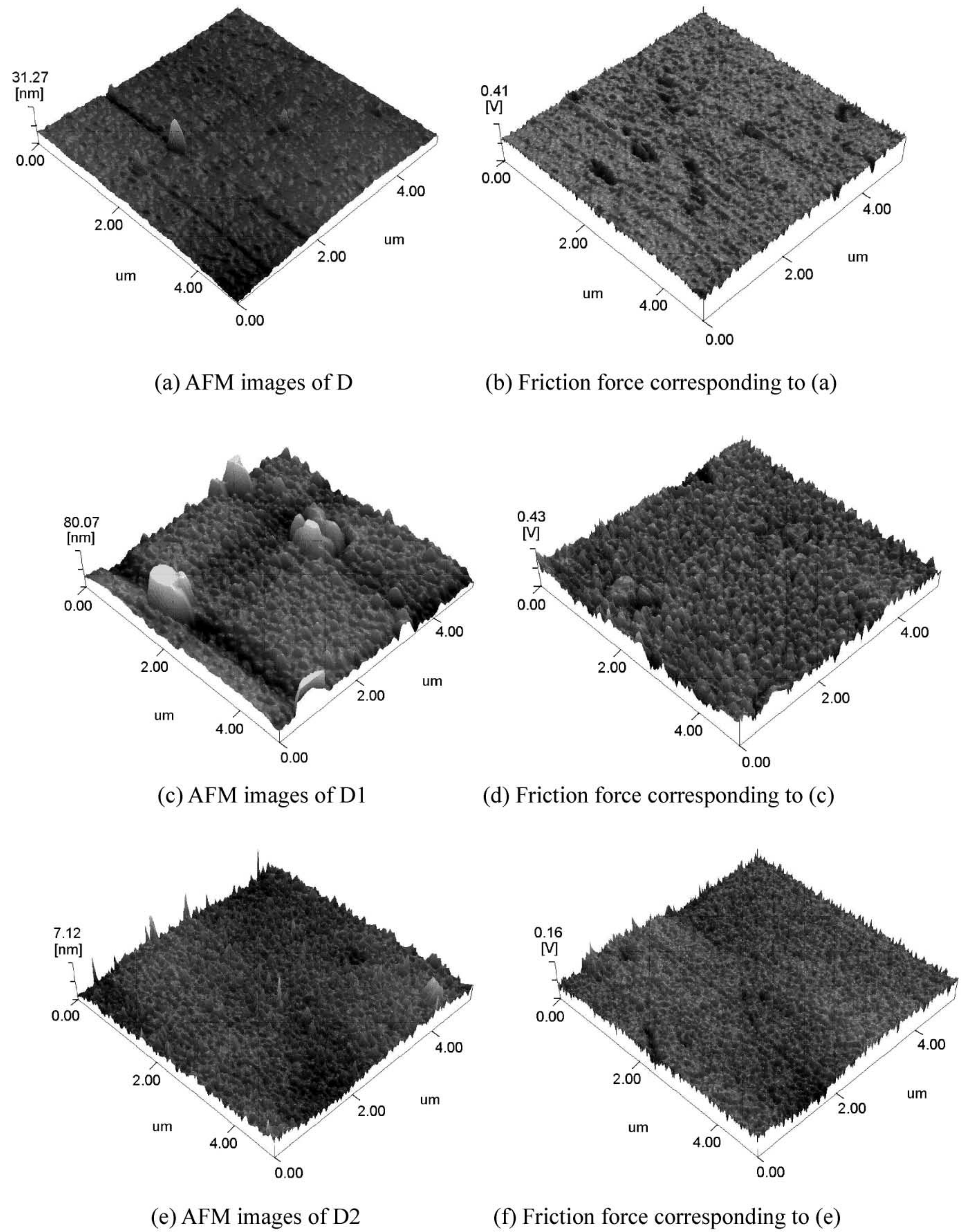
Fig. 1. XPS depth profile on the obtained Al_2O_3 (D) and Cu, Zn doped Al_2O_3 (D2) thin films.

sputtering cycles, which is certainly from the body film but not absorbed carbon. It is believed the detected carbon originates from the reactant burned in heating and then embedded in the film. This carbon may play a role in modifying the structure of the film. Fig. 1(b) gives the XPS depth profiles of Cu and Zn doped film (D2). As shown in Fig. 1(b), the peak of C_{1s} disappears after two cycles of sputtering, illustrating that contaminated carbon exists only on the very out surface of the film and the raw materials were completely converted or removed during the heating process. On the very out surface, the binding energy of Cu_{2p} at 934.5 eV is the signal of Cu_{2p} in $CuSiO_3$,[17] indicating that some solid reaction may have happened between the added CuO [original from the decomposition of $Cu(NO_3)_2 \bullet 5H_2O$] and the glass substrate. This phenomenon is also observed on the surface of Cu doped TiO_2 film,[6] confirming that this solid reaction did happened under the current sintering temperature. However, according to our previous result, the existence of $CuSiO_3$ is harmful to the wear life of the doped film. The binding energy 1021.7 eV of Zn_{2p3} is consistent with that of ZnO,[18] indicating that Zn exists in an oxide state.

Fig. 2 presents the AFM images of topography and corresponding friction forces of Al_2O_3 and doped Al_2O_3 films. It is seen that the surface of Al_2O_3 film is very smooth in appearance. Different from the above, the images of doped films show obvious differences, i.e., the surface of D1 film is rougher and shows signs of grown up particles while that of D2 film is much smoother. This reveals that the addition of inorganic salts changed the structure of the film to some extent, which is supposed to be related to the film growing process during sintering and the final existing state of the added elements. Moreover, it is also seen the corresponding images of friction forces are mimic to that of morphology, implying that the friction force is correlated with the surface morphology in much degree, which agree well with the previous result.[7] However, there is no exact correspondence between the morphology and the friction force yet as Fig. 2a–d shown. The surface of D1 is much rougher than that of D but the corresponding friction force is very close to that of D. This is very possibly because at atomic scale, friction is largely attributable to interfacial effects.[19] Surface forces, such as van der Waals force, hydration force, and electrostatic or double layer forces (depending on the materials), become dominant factor.[20] It is deserved to mention that D2 exhibits the smoothest surface and the lowest friction force at nano scale among all the tested films, which may be partly responsible for its better performance in reducing friction and wear as following discussed. In other words, the physical and chemical state of the surface of D2 is much different from that of the two others.

3.2. Friction and wear

The tribological properties of Al_2O_3 and doped Al_2O_3 thin films under different conditions are given in Fig. 3. It can be seen all the obtained films give much lower friction coefficients before failure compared with the glass substrate. At the same time, all the doped films are superior to Al_2O_3 film in resisting wear, which is different from the situation of TiO_2, where the addition of inorganic elements all decrease the wear life of the film significantly,[6] especially Cu doped TiO_2 film. This reveals that the effect of dope is closely correlated to the film preparation process as well as the composition and structure of the films. The wear life of all the films is ranked as $D2 > D1 > D$. For D, the friction coefficient increases only after several passes, illustrating which is too weak to resist wear in sliding against Si_3N_4. The friction curves are very similar to each other under higher (3N) and lower load (0.5N) in sliding against Si_3N_4. Roughly speaking, the wear life of the films is not dependent on the load. D2 exhibits the best tribological behavior, i.e., a very low friction coefficient and longer stable sliding process is obtained. It is reasonable to



(a) AFM images of D (b) Friction force corresponding to (a)

(c) AFM images of D1 (d) Friction force corresponding to (c)

(e) AFM images of D2 (f) Friction force corresponding to (e)

Fig. 2. AFM results on the as prepared film surfaces.

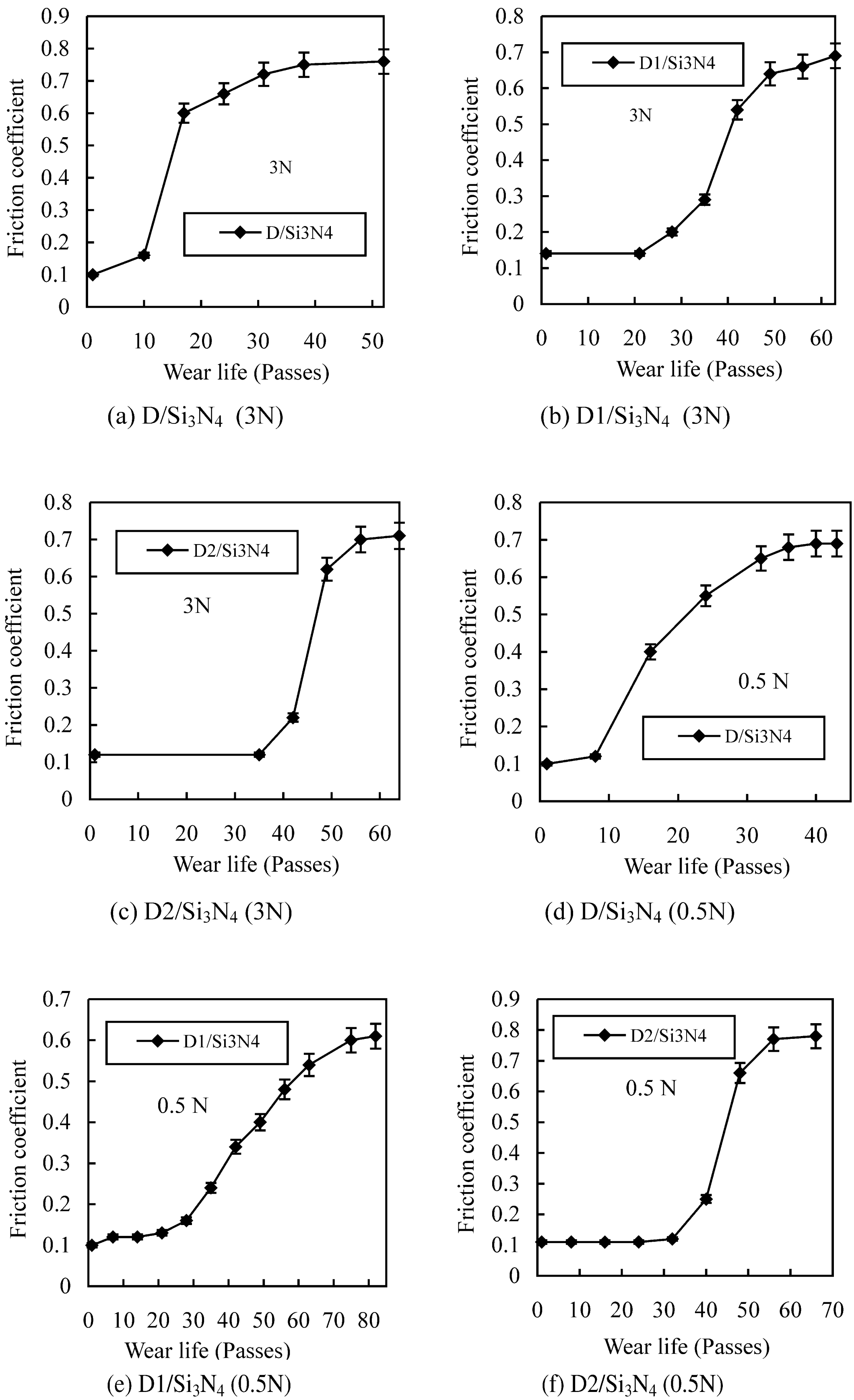
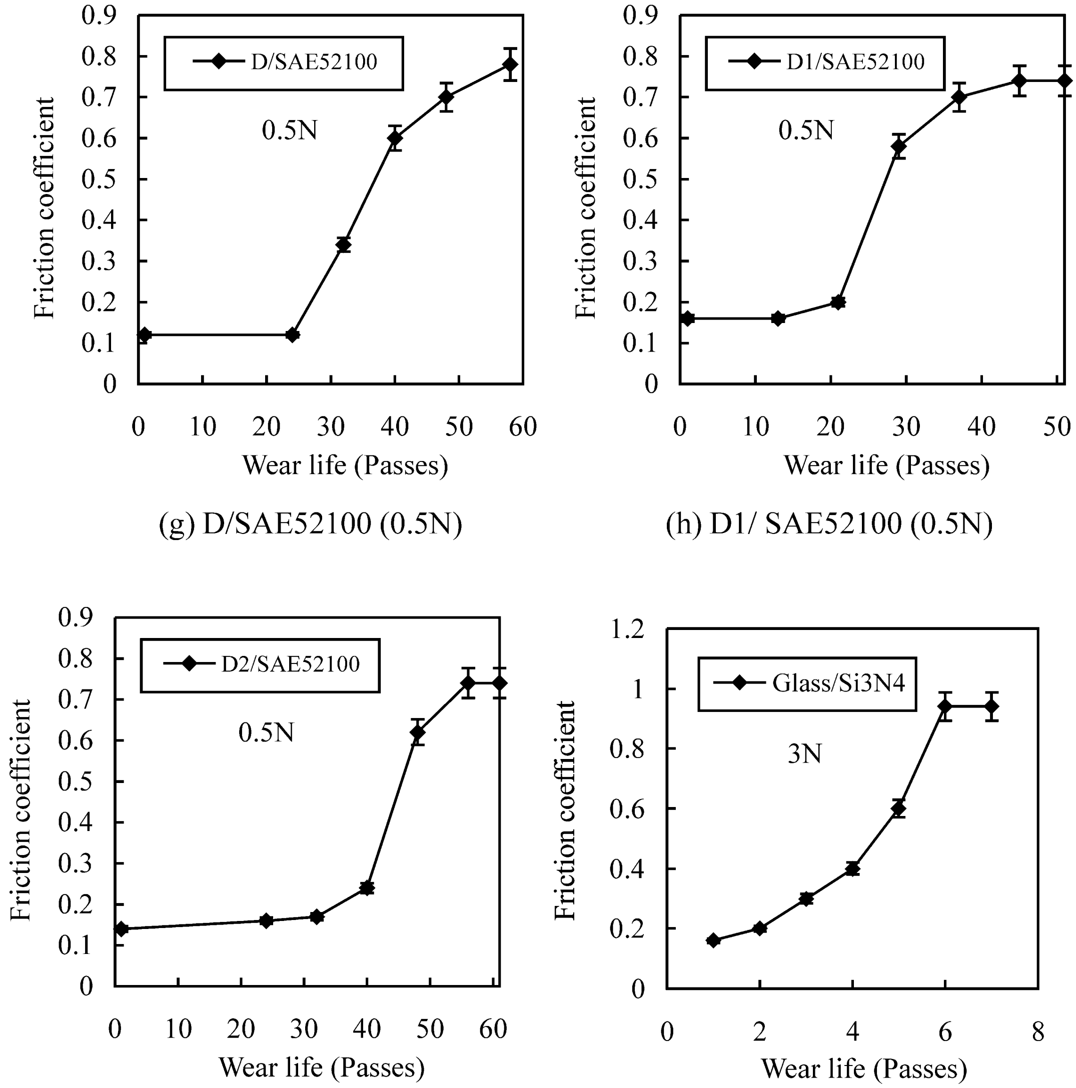


Fig. 3. Friction coefficients of different couples as a function of wear passes.



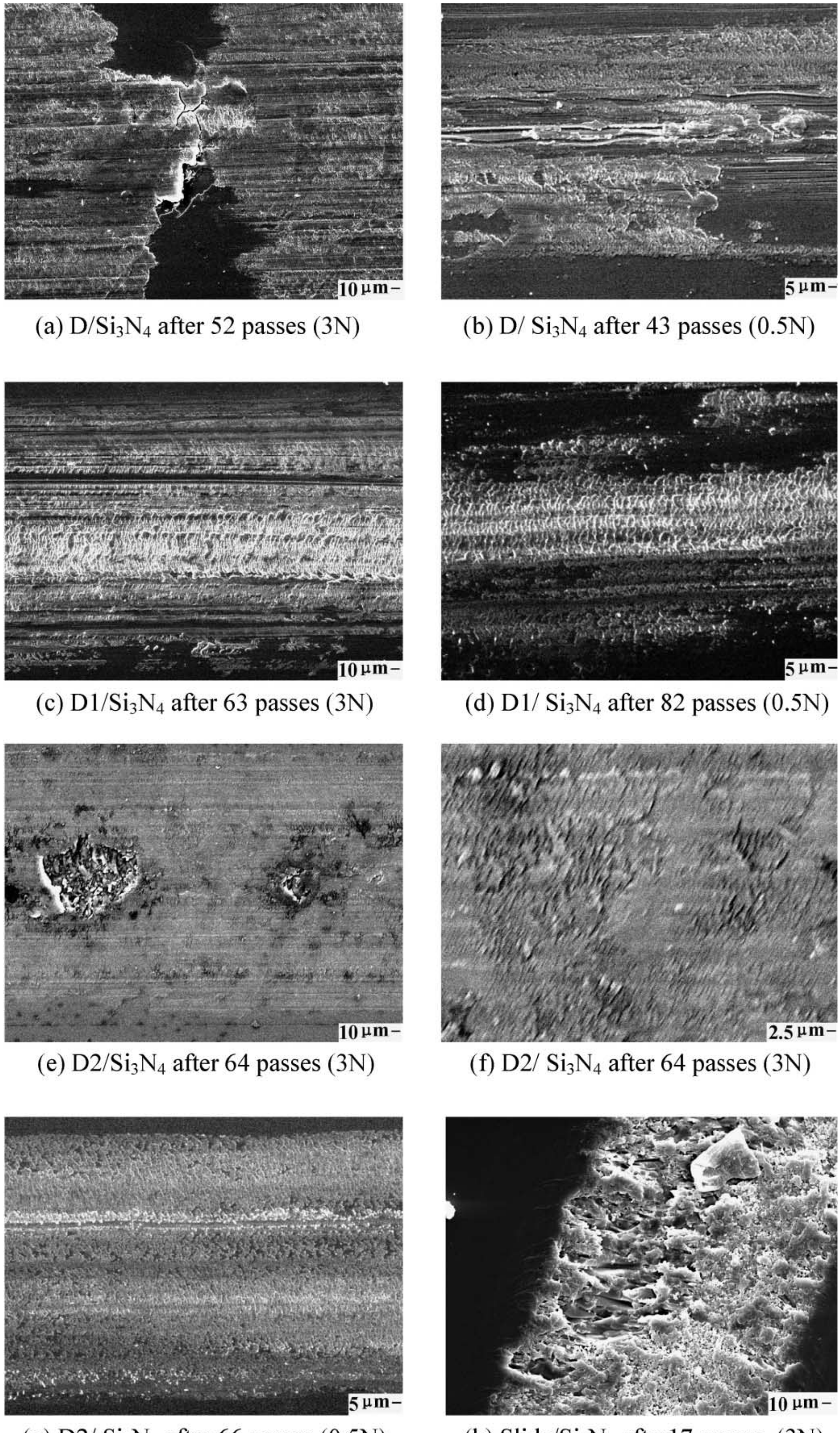
(g) D/SAE52100 (0.5N) (h) D1/ SAE52100 (0.5N)

(i) D2/ SAE52100 (0.5N) (j) Glass/ Si_3N_4 (3N)

Fig. 3. (continued)

infer that the better tribological properties of D2 is due to the introduction of ZnO which is helpful to improve the tribological property of Al_2O_3 film. It is interesting to point out that the wear life of D in sliding against the steel ball is elongated compared with that of D1 in the same condition and that of itself in sliding against Si_3N_4. Therefore, it is concluded that the wear life of the films is dependent on the sliding counterpart. For the glass slide, the coefficient of friction rises to a very high value (0.94) even after several passes, indicating that the glass slide has poor wear resistance.

To explore the friction and wear mechanisms of the films further, the worn surfaces of the obtained thin films and the glass substrate after sliding 17 passes sliding against Si_3N_4 have been observed by SEM. As shown in Fig. 4(a), sever brittle fracture happened on the surface of D, which led to the delamination of the film. At the same time micro-fracture are also observed. It is noted that both are responsible for the failure of film D. Under lower load (0.5N) the morphology of D is mimic to that under 3N, i.e., micro-fracture and delamination happened [Fig. 4(b)]. Different from the above, on the surface of D1, sever brittle fracture is avoided and plastic deformation is observed [Fig. 4(c)]. Under lower load, fracture and abrasive wear dominate the wear mechanism of D1 [Fig. 4(d)]. The worn surface of D2 is very smooth compared with that of D and D1 while a few fractures appeared [Fig. 4(e)]. In the mild wear area, creep can be clearly seen under high magnification [Fig. 4(f)]. Under lower load, abrasive wear has happened and the signs of plough are visible [Fig. 4(g)]. According to the above discussion it thus can be concluded the toughness of the doped films have been improved, which accounts for their better tribological



(a) D/Si_3N_4 after 52 passes (3N)

(b) D/ Si_3N_4 after 43 passes (0.5N)

(c) D1/Si_3N_4 after 63 passes (3N)

(d) D1/ Si_3N_4 after 82 passes (0.5N)

(e) D2/Si_3N_4 after 64 passes (3N)

(f) D2/ Si_3N_4 after 64 passes (3N)

(g) D2/ Si_3N_4 after 66 passes (0.5N)

(h) Slide/Si_3N_4 after17 passes (3N)

Fig. 4. SEM pictures of worn surfaces of obtained films and glass substrate sliding against Si_3N_4.

performance. As shown in Fig. 4(h), severe brittle fracture appears on the worn surface of the glass slide even after 17 passes, accompanied by the generation of large wear debris, which is responsible for the abrasive wear of the glass substrate and the resultant high friction coefficient.

Hence, it can be concluded that doping is an effective way to improve the tribological properties of the Al_2O_3 films even very little amount of dopant is added by avoiding sever fracture and delamination. However, the selected dopant is very crucial in modifying the tribological property of the film and leads to totally different results. Apparently, Zn element is more capable in improving the wear resistance of the film than Cu element in this study. According to the above discussion, both the superficial structure of the film and the existing state of the doped elements are partly responsible for their different tribological properties, ie. the surface of Cu doped film is rougher and shows signs of grown up particles while that of Cu, Zn doped film is much smoother. The essence of the results may relate to the generation of ZnO and $CuSiO_3$.

According to the SEM observation, it is supposed that the addition of the doped element may play a role in inhibiting the propagation of cracks during sliding. As a result, sever brittle fracture and delamination is avoided. This is why a longer wear life is obtained for the doped films.

4. Conclusion

Al_2O_3, Cu, and Cu, Zn doped Al_2O_3 films have been successfully obtained by sol-gel and dip-coating process. Results show that the addition of inorganic salts to the starting sol of Al_2O_3 can improve the tribological properties of the corresponding films. The wear life of the obtained films is ranked as Cu, Zn doped $Al_2O_3 > $ Cu doped $Al_2O_3 > Al_2O_3$. The tribological performance of the films is sensitive to the sliding counterpart but not the applied load in this text. A very low friction coefficient of around 0.1 is obtained for all the films. The failure of the film is mainly due to its brittleness.

The effects of the dopants on the tribological property of the film are closely related to the generated compounds from the inorganic salts as well as the characteristics of the generated surfaces. The avoidance of the sever fracture and delamination is partly responsible for the corresponding longer wear life of the doped films according to the SEM observation. The introduction of ZnO is recommended to improve the tribological property of Al_2O_3 film.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 59825116). They are also grateful to Engineer Shang-kui Qi and Ping-yu Zhang for their assistance in XPS and AFM analyses.

References

1. Dislich, H., *J. Non-Cryst. Solids*, 1983, **57**, 371.
2. Hirai, S., Shimakage, K., Sekiguchi, M., Wada, K. and Nukui, A., *J. Am. Ceram. Soc.*, 1999, **82**, 2011.
3. Ershad-Langroudi, A., Mai, C., Vigier, G. and Vassoille, R., *J of Applied Polymer Science*, 1997, **65**, 2387.
4. Paterson, M. J., Paterson, J. K. and Ben-Nissan, B., *J. Mater. Res.*, 1998, **13**, 388.
5. Jamting, A. K., Bell, J. M., Swain, M. V., Wielunski, L. S. and Clissold, R., *Thin Solid Films*, 1998, **332**, 189.
6. Zhang, W. G., Liu, W. M., Li, B. and Mai, G. X., Characterization and tribological investigation of sol-gel TiO_2 and doped TiO_2 thin films. *J. of Am. Ceram. Soc.*, in press.
7. Zhang, W. G., Liu, W. M. and Xue, Q. J., *Mater. Res. Bull.*, 2001, **36**, 1903.
8. Donnet, C., *Surface and Coating Technology*, 1998, **100–101**, 180.
9. Donnet, C. and Grill, A., *Surface and Coating Technology*, 1998, **94–95**, 456.
10. Lin, H., Kumon, S., Kozuka, H. and Yoko, T., *Thin Solid Films*, 1998, **315**, 266.
11. Joo-Sin, L., Matsubara, T., Sei, T. and Tsuchiya, T., *J. Mat. Sci.*, 1997, **32**, 5249.
12. Juodkazis, S., Bernstein, E., Plenet, J. C., Bovier, C., Dumas, J., Mugnier, J. and Vaitkus, J. V., *Thin Solid Films*, 1998, **322**, 238.
13. Imai, H. and Hirashima, H., *J. Am. Ceram. Soc.*, 1999, **82**, 2301.
14. Deshkovskaya, A. A. and Richter, E., *Surface and coating technology*, 1997, **93**, 150.
15. Barna, P.B. and Pauleau, Y., In *Protective Coatings and Thin Films*. NATO-ASI Series 3. High Technology Vol. 21. Kluwer, Dordrecht, 1997, p. 659.
16. Wagner, C. D., Passoja, D. E., Hillery, H. F., Kinisky, T. G., Six, H. A., Jansen, W. T. and Taylor, J. A. J., *Vac. Sci. Technol*, 1982, **21**, 933.
17. C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Mullenberg, *Handbook of X-ray Photoelectron Spectroscopy*. Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, MN 55344, 1979.
18. Schoen, G. J., *Electron Spectrosc. Relat. Phenom*, 1973, **2**, 75.
19. Krim, J., *Langmuir*, 1996, **12**, 4564.
20. Hsu, S. M., *Langmuir*, 1996, **12**, 4482.