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Effects of solvents on the tribological behaviour of sol–gel Al_2O_3 films

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Abstract

Thin films of Al_2O_3 and modified Al_2O_3 were prepared on a glass substrate by dip coating process from specially formulated aqueous/ethanol sols. Thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC) of precursor gels were performed to explore the thermal events occurring during the annealing process of the sol–gel Al_2O_3 films. The morphologies of the unworn and worn surfaces of the films were analyzed by atomic force microscope (AFM) and scanning electron microscopy (SEM). The chemical composition of the film was characterized by X-ray photoelectron spectroscopy (XPS). The tribological properties of the films sliding against Si_3N_4 ball were evaluated on a one-way reciprocating friction and wear tester. AFM and XPS results confirm that the solvents can influence the structure and composition of the film significantly. The film from ethanol solution process shows longer wear life than the one from distilled water solution, especially under lower load. The added polyethylene glycol (PEG) modifier in sols generates totally different effects on the tribological behaviour of the films with respect to solvents. The addition of PEG to ethanol solution deteriorates the wear resistance of the corresponding film. Differently, the wear resistance of the modified film from aqueous solution is significantly improved. Actually, the modified film from water solution shows the best wear resistance among all the films. The wear mechanisms of the films are discussed based on SEM observation of the worn surface morphologies. Results show that brittle fracture and severe abrasion dominates the wear of glass substrate. The wear of the film from aqueous solution is characteristic of micro-fractures, the corresponding modified film shows better plasticity and fewer micro-cracks, whereas, the wear of the film from ethanol solution was characterized by abrasive and slight plastic deformation, and the corresponding modified one shows evidence of abrasive and brittle fracture.

Keywords: D. Al_2O_3; Sol–gel films; Solvents; Tribological behaviour

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 or electrical material.

It is known the preparation processes are very critical in modifying the properties of the sol–gel ceramics [6–11]. Many factors, such as the solvents [7,8], dopants [9] and modifiers [10,11] are very decisive. We once investigated the effect of the modifier polyethylene glycol (PEG) on the tribological properties of Al_2O_3 from

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aqueous solution. It is found the modifier is effective in improving the tribological property of the sol–gel film. The best tribological property of Al_2O_3 is obtained while the addition amount of PEG is 0.6% [12]. It is also found out that the dopants are very influential on the tribological properties of the Al_2O_3 films in our previous work [13]. However, the effect of another very important factor-solvent is not investigated yet.

In this study, we report on the fabrication of Al_2O_3 and modified Al_2O_3 thin films by the sol–gel process, particular attention being paid to the effect of the solvents on the tribological behaviours. PEG is generally used as a binder. The effect of PEG with respect to solvent is also discussed. The addition amount of PEG 0.6% is chosen according to the previous result. Two most popularly used solvents-distilled water and ethanol in preparing sols are chosen in this study. According to film composition and structure the friction and wear mechanisms of the films are also discussed in detail based on the SEM observation of the worn surface morphologies.

2. Experimental

2.1. Sample preparation

For the preparation of the aqueous and ethanol sols, commercial crystal aluminum chloride (99.99%), ammonia, glacial acetic acid and polyethylene glycol (abridged as PEG: a kind of binder used to improve the toughness of the sol–gel ceramic film, $M_w = 400$) was used without further purification. Excess ammonia solution (5 M) was added dropwise at room temperature to an aqueous aluminum chloride solution (0.13 M) of 100 ml. The final pH value of the solution was 9. The resultant hydrated precipitate was filtered, washed with pure water and ethanol respectively, aged for 2 days. The obtained gels were then peptized with glacial acetic acid (room temperature for 3.5 h under stirring) in distilled water and ethanol, respectively, to obtain translucent, homogeneous, and corresponding stable sols A and C. The final pH of the solution was about 4$\sim$5. The corresponding modified solutions of A and C (coded as A3 and C1 respectively) were obtained by adding 0.6 ml of PEG to 100 ml of the A and C solutions, respectively. The resultant solution was aged for 24 h and served as the coating solution.

The glass substrate (composition: SiO_2 80.5%, B_2O_3 12.9%, Na_2O 3.8%, Al_2O_3 2.2% and K_2O 0.4%) was firstly cleaned with ethanol-potassium hydroxide solution in an ultrasonic bath for 20 min, then washed with distilled water and dried at ambient conditions. Sol–gel Al_2O_3 films were prepared on the glass substrate by a dip-coating process. This was realized by drawing and pulling the substrate in the corresponding sols at a speed of 38 cm min^{-1}, at room temperature drying for 15 min and annealing at 500 °C for 20 min in an oven. The target sol–gel Al_2O_3 films were finally obtained by cooling the glass substrate to ambient temperature in the oven.

2.2. Experimental apparatus and measurements

The composition and structure of the films were characterized by TGA, DSC, XPS and AFM. DSC and TGA analyses were performed in nitrogen on a Perkin-Elmer DSC-7 and TGA-7 system at one heating rate of 10 °C min^{-1}. The samples used for thermal analysis were obtained by evaporation of the precursor solutions at room temperature for 72 h. XPS analysis was conducted on a multi-functional XPS/AES system (Model PHI-5702) 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 by Ar^+ ion bombardment with a beam voltage of 2 kV, a beam density of 6 nA cm^{-2}, and a sputter area of 1×1 mm. The surface morphology of the thin films was observed by an atomic force microscopy (AFM) (Model SPM-9500). The original and worn surfaces of the films were observed via SEM (Model JSM-5600LV).

The tribological properties of the glass and of the coated glass sliding against a stationary ball (diameter 3 mm, made of Si_3N_4) were evaluated on a Kyowa DF PM model one-way reciprocating friction and wear tester at ambient conditions (RH: 40$\sim$44%). The sliding velocity and stroke were 90 mm min^{-1} and 7 mm, respectively. The normal force is selected as 3 and 1 N, in anticipation that the sol–gel Al_2O_3 films would experience failure above a normal force 3 N because of the excessive Hertzian contact stress. The physical and mechanical properties of the counterpart Si_3N_4 ball are shown in Table 1. The coefficient of friction and sliding passes were recorded automatically. A relatively low friction coefficient was recorded at the early stage of sliding. It rose sharply to a higher stable value after sliding for a certain passes. It is usually recognized that the film fails at this point. Therefore the corresponding sliding pass numbers were recorded as the wear life of the film. Three replicate tests were carried out for each specimen, i.e. A, C, A3 and C1, and the average friction coefficients and wear lives of the three replicate tests are reported. 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.

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

3. Results and discussion

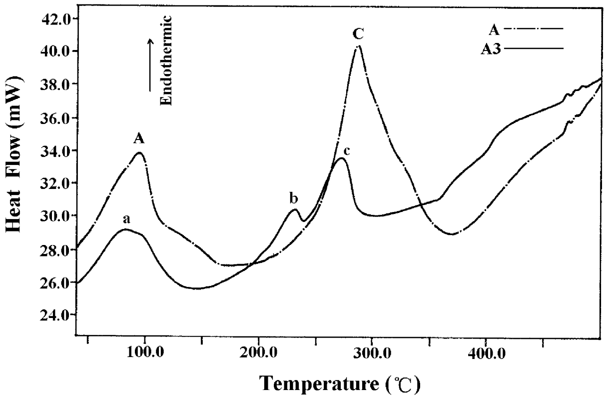
3.1. Characterization of film precursor

It is supposed that the solvents will affect the film formation process, which can be explained according to their different thermal behaviour during annealing. Figs. 1 and 2 show the DSC and TGA analytical results of film precursors of A, A3 and C, C1. Here, more attention is paid to the effects of modifier on the thermal behaviour of the film precursors with respect to the solvents. For convenience, A (a), B (b), C (c), and D (d) sign the peaks, respectively. The same letter in upper case and lower case is used to describe the peaks in close position.

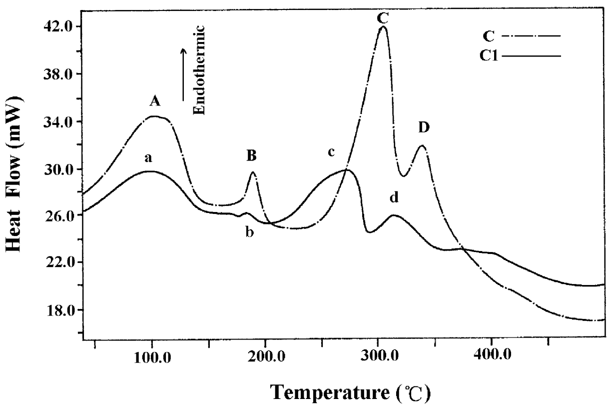
Fig. 1(a) shows the DSC resultant curves of A and A3. Precursor A shows two endothermic peaks, while precursor A3 shows three endothermic peaks. A peak (A/a) appears around 90 °C for both A and A3, indicating that the two precursors experience the same process at this temperature. A new peak b appears for A3, which is due to the loss of coordinated water related to the modifier. The second process (C/c) for A is delayed as compared with A3, indicating that the second process is easier to happen for A3. This is supposed to be related to the action of the organic additive, which may act as a cross-linker, i.e. PEG favors the molecules cross-linking and enhances the formation of Al_2O_3 particles in the subsequent heating process.

Fig. 1(b) shows the DSC curves for C and C1. The first endothermic peak around 100 °C for C and C1 is very similar to that of A and A3 due to the removal of free solvents. Compared with A and A3, the most significant difference lies in that a new peak (B/b) appears around 150∼200 °C. This is possibly due to the removal of chemically absorbed ethanol on the gel particle surface. It is known that abundant –OH radicals exist on the surface of Al_2O_3 gel as Al–OH, which can form strong hydrogen bond with hydroxyl in ethanol. The peak C/c is due to the loss of coordinated water related to ethanol or PEG. The difference between C and c is that the peak for PEG appears in lower temperature. Similar phenomenon is also observed on peak D/d. This indicates that PEG still plays some role in the situation of C1 but the effect may be weakened by the existence of ethanol.

Fig. 2 shows the TGA resultant curves of the precursors. The greatest weight loss observed between 200 °C and 300 °C, which is very similar for A, A3 and

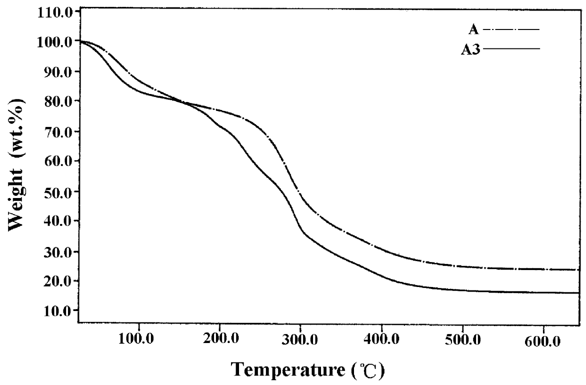


(a) DSC of A and A3

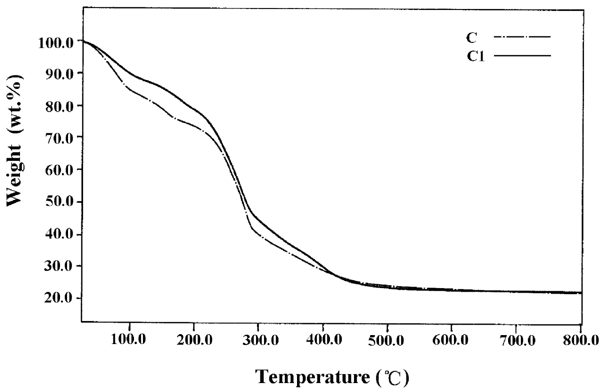


(b) DSC of C and C1

Fig. 1. Results of DSC analysis on the film precursors.



(a) TGA of A and A3



(b) TGA of C and C1

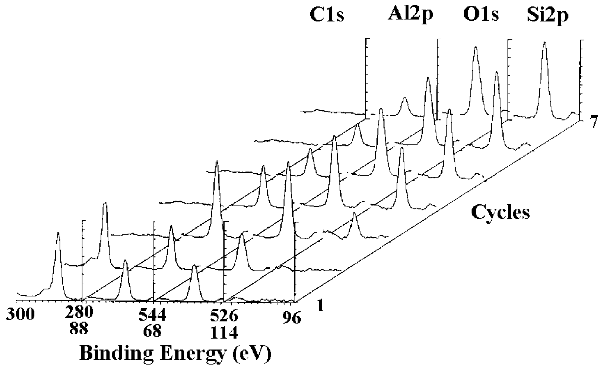
Fig. 2. Results of TGA analysis on the film precursors.

C, C1, is mainly due to the formation of Al–O–Al structure and the loss of corresponding coordinated water. The weight loss of A3 is apparently larger than for A, which can be explained PEG being easily absorbed on the surface of the precursor particles due to the strong polarity of hydroxyl. The loss of organic compound or more coordinated water thus accounts for the difference between A and A3. However, C and C1 record almost the same weight losses. This is very understandable by considering that both ethanol and PEG have hydroxyls, which endue them similar adsorption behaviours. The role of PEG as a cross-linker herein is weakened. This further confirms that the different adsorption behaviours of the modifier generate different effects on A3 and C1. As a result, different tribological behaviours of A3 and C1 are also obtained as discussed below.

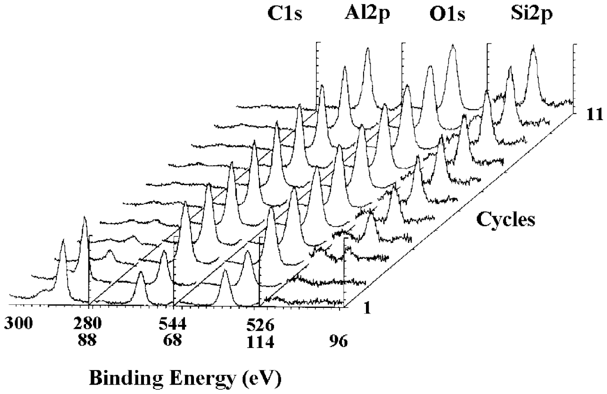
According to the above, it can be concluded that addition of organic additives can modify the film formation process, which thereby changes the structure of the film. Concretely, the states of micelles in water and ethanol should be different from each other because of the different polarities of water and ethanol whilst the existence of PEG enables the particles in sol cross-link with each other easily. As cross-linker, PEG is more effective than ethanol due to the more hydroxyls being attached to PEG. The presence of ethanol may weaken the effect of PEG due to the absorption of ethanol on the surface of micelles as well as the interaction between PEG. Moreover, PEG may also play a role in modifying the adhesion behaviour of the sol on the surface of the glass substrate due to its polarity.

3.2. Characterization of the film

Fig. 3 shows the XPS depth profiles of film A and C. The binding energy of Al_{2p} on the very outer surface of A and C is 74.20 and 74.30 eV, respectively, which is consistent with that of Al in sapphire Al_2O_3 [14]. This indicates that the target Al_2O_3 film can be successfully obtained regardless of the solvents. However, differences also appear on the profiles of film A and C. Most apparently, the peak of C_{1s} on the surface of A disappears after two cycles of sputtering, which is due to the contaminated carbon, existing only on the very outer surface. Differently, C_{1s} peak on the surface of C still exists even after five sputtering cycles, which derives certainly from the body film but not from absorbed carbon. This further confirms that ethanol was easily chemically absorbed on the surface of the micelles, which was then burned while heating and embedded in the film. This carbon is supposed to play some role in modifying the structure and tribological properties of the films. Moreover, it can be found that the intensity of Al_{2p} in the profile of A becomes very weak after seven sputtering cycles, while the intensity of Al_{2p} in the profile of C is still strong even after 11 sputtering cycles. It is thus inferred that film C is thicker than film A, which may derive from the different polarity of ethanol and water, ie., ethanol with hydroxyl adheres easily on the surface of the glass substrate. This may also partly accounts for the different tribological properties of A and C.



(a) Profile of A

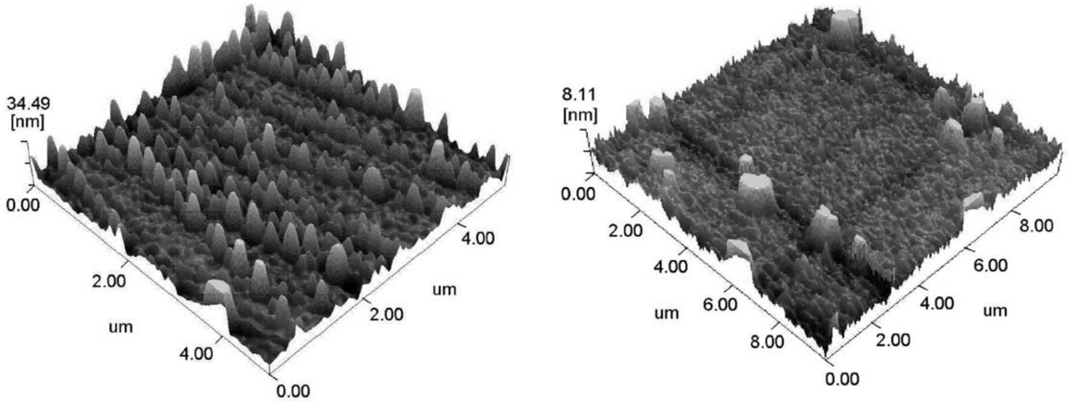


(b) Profile of C

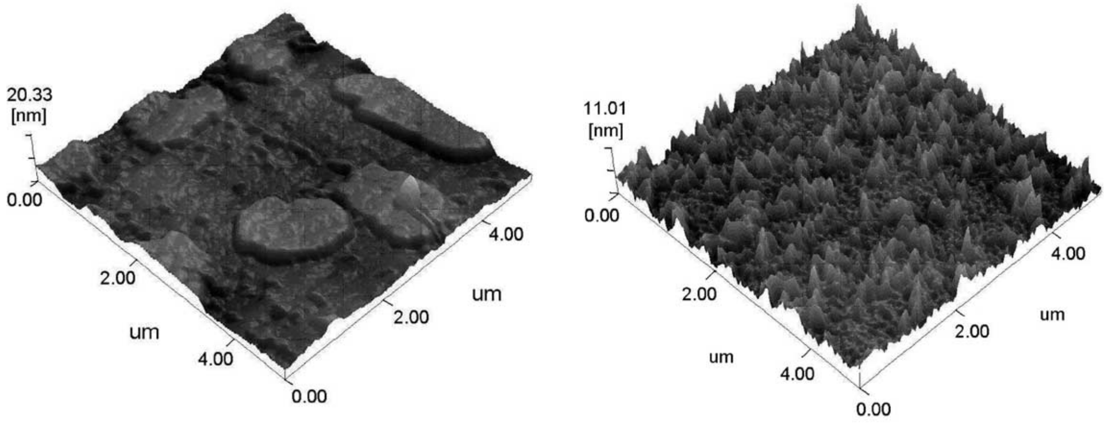
Fig. 3. XPS depth profiles on the sol–gel Al_2O_3 thin films.

Fig. 4 shows the AFM images of the films. Water and ethanol solvents also show some effects on the surface morphology of the films. For film A, the grown-up nano-sized particles arrange in specific orientation, indicating that the growth of Al_2O_3 particles herein is accompanied by a preferential orientation. The surface of film C is relatively smoother with a few larger particles.

The effects of the added modifier on the surface morphology of the films are also different with respect to the solvents. For film A3, the surface becomes smooth and takes the shape of some “island” distributed in “marshland”. This indicates that the addition of PEG may play a role as cross-linker connecting the particles in growing process. As a result, “islands” appears. This structure is supposed to be helpful in inhibiting the propagation of the cracks caused by friction stress as discussed below. Differently, the surface of film C1 is rougher than that of C and no “islands” appears.



(a) AFM image of A (b) AFM Image of C



(c) AFM image of A3 (d) AFM Image of C1

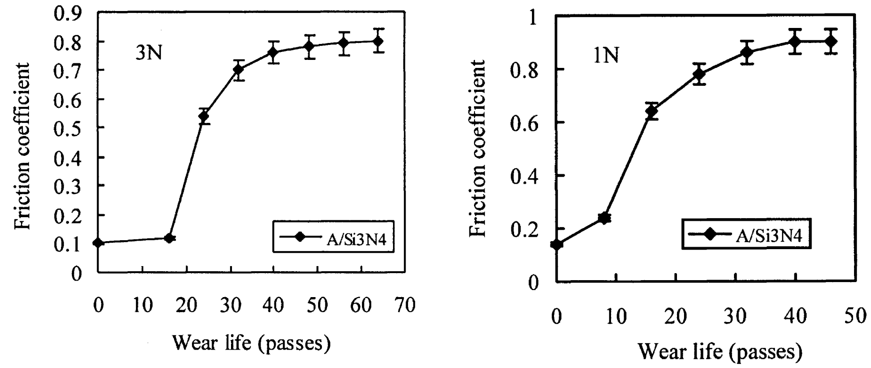
Fig. 4. AFM images of prepared Al_2O_3 thin films.

3.3. Friction and wear behaviour

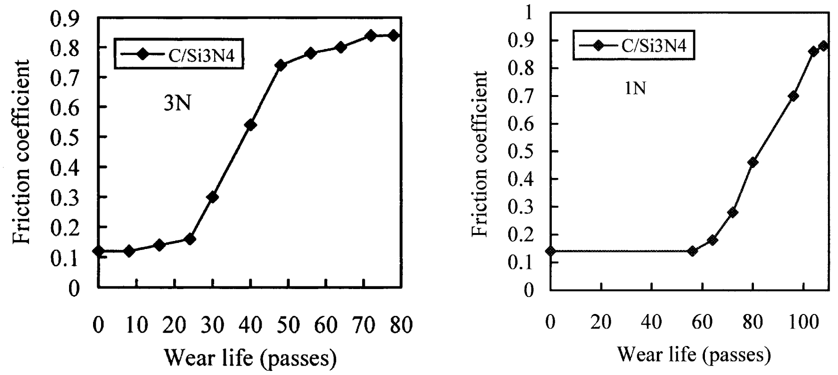
Fig. 5 shows the friction coefficients of the couples as a function of the wear passes. The wear life of A is very short both under 3 and 1 N [Fig. 5(a) and (b)]. Compared with A, C shows longer wear life, especially under lower load 1 N [Fig. 5(c) and (d)]. Moreover, the friction coefficient for C at 1 N is more stable. This is understandable considering that the structures and compositions of these two films are different. Concretely, the embed carbon may improve the toughness of film C. Moreover, C is thicker than A and the surface of C is smoother than that of A, which are all possibly responsible for the better tribological performances of C.

Very interestingly, the wear life of corresponding modified film of A, i.e. A3, is greatly improved also under 3 N, which even registers a wear life above 9736 passes under lower load ($\leqslant 1$ N) [Fig. 5(e) and (f)]. This is very possibly due to the improved toughness of the film caused by the addition of the modifier. Differently from A3, C1 shows shorter wear life than C, ie., the addition of PEG to ethanol solution seriously deteriorates wear resistance of C [Fig. 5(g) and (h)]. This reveals that the modifier play a totally different role on the tribological performances of the films with respect to the solvents. Even so, most of the films show better wear resistance than the glass substrate. For the glass substrate, the friction coefficient increases to a very high value only after several passes.

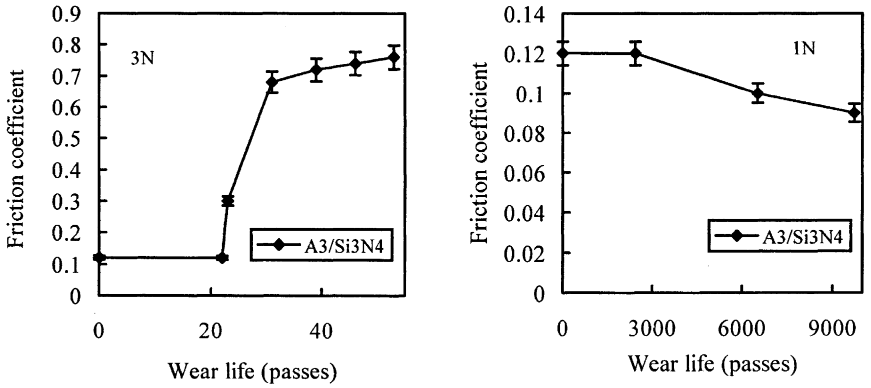
To explore the friction and wear mechanisms further, the worn surfaces of the glass substrate after 17 passes and Al_2O_3 thin films after failure sliding against Si_3N_4 have been observed by SEM. As shown in Fig. 6, the signs of severe brittle fracture are visible on the worn surface of the glass slide even after 17 passes [see Fig. 6(a)], accompanied by the generation of large particles, which accounts for the abrasive wear of the slide and the resultant high friction coefficient. Differently, many micro-cracks generated on the worn surface of film A. The propagation of these cracks then causes micro-fracture and leads to film failure in a relatively short sliding duration. Contrary to the above, the worn surfaces of film A3 show signs of slight plastic deformation, which is beneficial to prevent the generation of



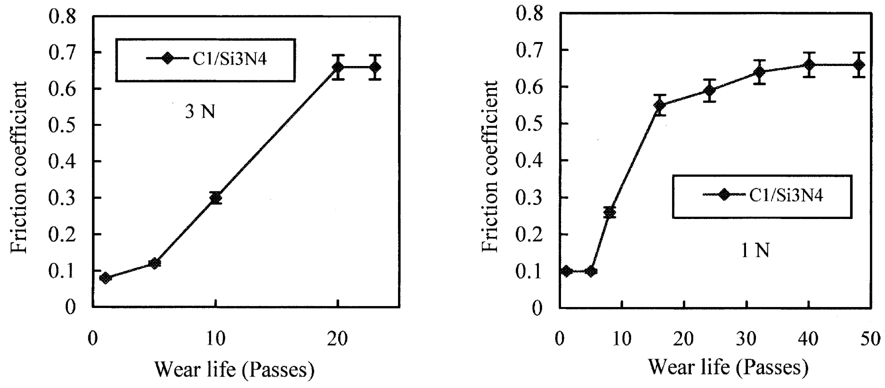
(a) Al_2O_3 (A)/Si_3N_4 (3N) (b) Al_2O_3 (A)/Si_3N_4 (1N)



(c) Al_2O_3 (C)/Si_3N_4 (3N) (d) Al_2O_3 (C)/Si_3N_4 (1N)

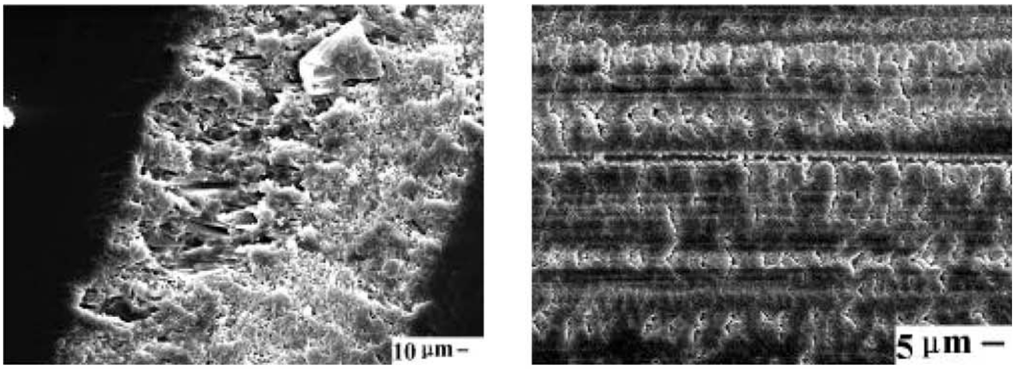


(e) Modified Al_2O_3 (A3)/Si_3N_4 (3N) (f) Modified Al_2O_3 (A3)/Si_3N_4 (1N)

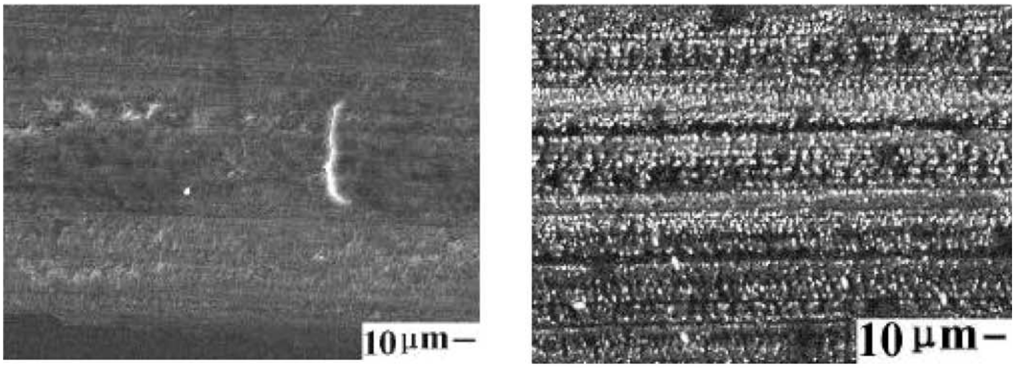


(g) Modified Al_2O_3 (C1)/Si_3N_4 (3N) (h) Modified Al_2O_3 (C1)/Si_3N_4 (1N)

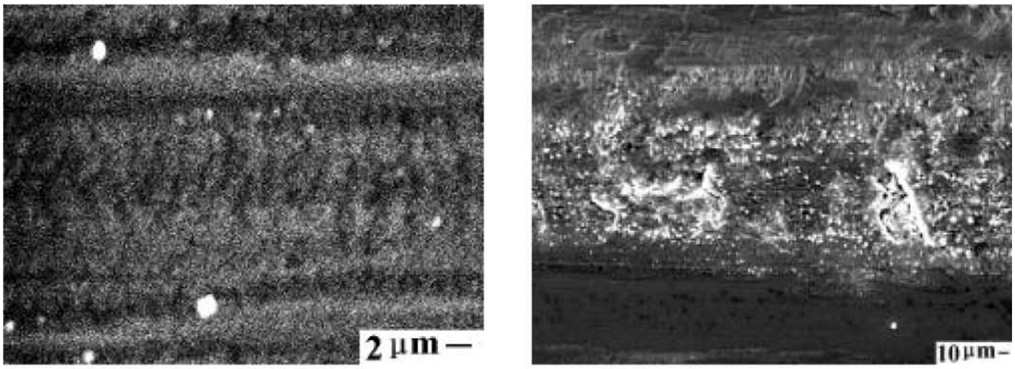
Fig. 5. Friction coefficients of different couples as a function of wear passes near to failure.



(a) Glass slide /Si_3N_4 (3N) (b) Al_2O_3 (A) /Si_3N_4 (3N)



(c) Al_2O_3 (A3) /Si_3N_4 (3N) (d) Al_2O_3 (C) /Si_3N_4 (3N)



(e) Al_2O_3 (C) /Si_3N_4 (1N) (f) Al_2O_3 (C1) /Si_3N_4 (3N)

Fig. 6. SEM pictures of worn surfaces of glass substrate after 17 passes, Al_2O_3 and modified Al_2O_3 thin films after failure sliding against Si_3N_4.

micro-cracks. In other words, film A3 of higher roughness shows better wear-resistance than film A of lower roughness. It is rational to anticipate that film A3 would be a promising candidate for protection and wear reduction of micro-devices in relatively low-load applications.

Different from A, large quantities of fine abrasive particles appears on the worn surface of C [see Fig. 6(d)], indicating that abrasive wear happened. Under high magnification slight plastic deformation appears at 1 N [see Fig. 6(e)]. This may partly accounts for the longer wear life of C. On the worn surface of C1 not only abrasive particles but also brittle fractures are visible [see Fig. 4(f)], which accounts for the deteriorated wear resistance of C1.

To summarize, the solvents can influence the structure and composition of the films significantly. As a result, film A and film C show much different tribological behaviours. It is also deserved to note that the effect of the modifier on the tribological behaviour of the films is also dependant on the solvents.

4. Conclusions

Al_2O_3 thin films derived from special formulated aqueous and ethanol solutions have been produced. It is found the solvents play a crucial role in determining the morphology and correspondingly the tribological performances of the films. The film from ethanol solution shows longer wear life than the one from aqueous solution, whereas the modified one from aqueous solution shows much better wear resistance than the one from ethanol solution. The addition of PEG in ethanol solution deteriorates the wear resistance of resultant modified film, while the action of PEG in the aqueous solution is beneficial for the tribological performance of the resultant film.

It is thus concluded that a process starting from aqueous solution with modifier PEG and a process from ethanol solution without modifier PEG is recommended for the preparation of Al_2O_3 sol–gel films. It is also noted that by choosing appropriate solvents and modifiers the sol–gel method could prove suitable for preparing thin ceramic films with good tribological performances.

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