Abrasive wear of thick silica films prepared by vacuum evaporation

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We investigate the wear behaviour of thick silica films 2–3 μm thick evaporated on a polymethylmethacrylate substrate in vacuum. The wear test is performed with kaolin mineral powder suspended in water. Abrasive wear is not affected by silica film hardness varying from 100 to 550 kg mm^{-2}, which corresponds to film preparation pressures ranging from 5×10^{-3} to 5×10^{-5} torr. The wear characteristics and the appearance of the wear tracks are strong evidence that abrasive wear of the deposited silica films consists of the mechanical and molecular removal of a hydrolysed silica film surface by abrasive kaolin grains. This is very similar to the case of glass polishing.

1. Introduction

Evaporated silica films have found a wide variety of uses in optical and electronic devices: optical thin films, interference filters, protective films for mirrors and insulating films for thin film devices. Extensive studies have been made of the optical and electrical properties of evaporated silica films, but their mechanical properties, e.g. wear, friction and adhesion have not been well investigated, notwithstanding their importance as protective or hard coatings; this may be because of the difficulty of making measurements and interpretating the results.

In the present study we have investigated the abrasive wear of vacuum-deposited thick silica film hard coatings on polymethylmethacrylate (PMMA) substrates. The abrasive wear of a material is caused, in principle, by friction between that material under test and a harder body or grains of harder minerals as abrasive.

Kruschov [1] in his review of the mechanism of abrasive wear reported that wear increases with increasing hardness and modulus of elasticity of the material. We have previously studied microhardness of thick SiO_2 films in relation to film deposition conditions and composition [2] and found that the film hardness varied from 150 to 620 kg mm^{-2} depending on the vacuum pressure. So we expect the abrasive wear of deposited SiO_2

films to be a function of hardness, if Kruschov's view is taken into account.

Another aspect to be considered is the expected chemical or mechanicochemical properties of the abrasive grains, the material under friction and the lubricating medium, which depend on their chemical composition.

This study aims at clarifying the abrasive wear and wear mechanism of thick deposited silica films on PMMA under wear with kaolin abrasive powder suspended in water.

2. Experimental details
2.1. Sample preparation

Silicon monoxide (SiO) was evaporated in vacuum by the normal resistance heating method. The substrate was polymethyl methacrylate plate several mm thick. The pressure at deposition ranged from 2×10^{-10} to 5×10^{-5} torr, and the source–substrate distance from 10 to 24 cm. The deposition rate was 0.5 to 1.7 μm min^{-1} and the film thickness varied from 0.5 to 5 μm.

2.2. The wear test

The wear tester was constructed as shown schematically in Fig. 1. The wear data were always obtained from tests on three or four specimens. Kaolin powder of about 15 μm particle size was suspended in water and stirred. The concentration
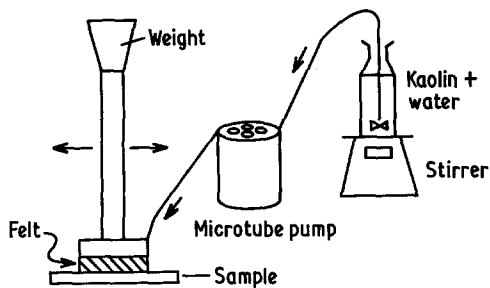
Figure 1 Wear tester.

Figure 2 Wear depth versus silica film thickness. Pressure 500 g cm^{-2}; 2000 runs.

was 2.5 g kaolin in 50 cm^3 water. The slurry was fed continuously from the feeder on a wool felt at a rate of $1.3 \text{ cm}^3 \text{ min}^{-1}$.

The silica-film coated specimen fixed on the bed was abraded at a pressure of 500 kg cm^{-2} by the felt abrader reciprocating unidirectionally at 35 runs min^{-1} over a span of 4 cm and simultaneously shifted at a speed of 1 mm min^{-1} perpendicularly to the direction of abrasion to obtain homogeneous wear. In all experiments each specimen was worn by 2000 abrasion runs.

The degree of abrasive wear for the silica film was determined by X-ray fluorescence analysis. We measured the initial thickness of the evaporated SiO_2 film with a surface profile meter before wear, and the corresponding X-ray fluorescent intensity of silicon in the film. We again measured the X-ray intensity of silicon for the worn SiO_2 film and, neglecting the X-ray absorption effect of the film itself, we easily calculated the mean wear depth for 2000 runs of abrasion from the initial film thickness value.

2.3. Microhardness
The Vickers microhardness of the films was determined using a commercial hardness tester under a load of 25 g for a loading time of 30 sec. To obtain genuine hardness values, SiO_2 films over $7 \mu m$ in thickness were used. Since the kind of substrate material makes no difference [3] for films of thickness greater than $7 \mu m$, we used SiO_2 films deposited on a commercial glass plate substrate throughout the film hardness measurements.

3. Results and discussion
3.1. Film thickness and abrasive wear
The effect of film thickness on abrasive wear was investigated first on silica films on a PMMA substrate. The films were deposited under a pressure of 5×10^{-4} torr with a deposition rate
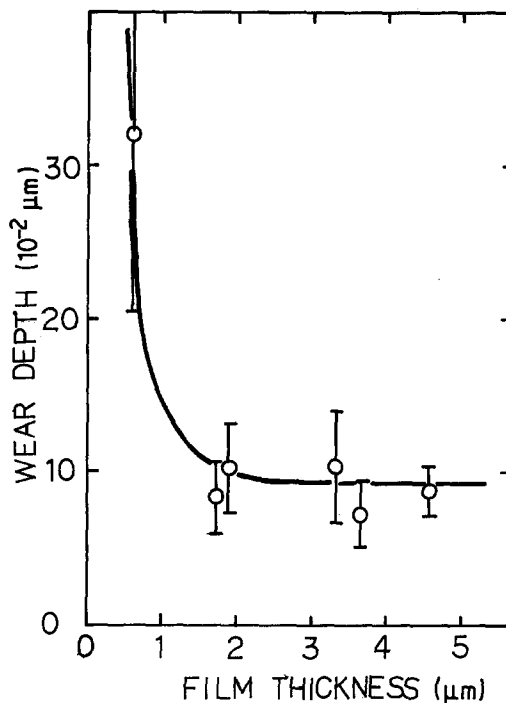
of $1 \mu m \text{ min}^{-1}$ for a source–substrate distance of 17 cm.

Fig. 2 shows the relationship between the thickness and abrasive wear depth of the films. Wear of a SiO_2 film $0.6 \mu m$ thick gives a high wear depth of $30 \times 10^{-2} \mu m$ and the wear depth decreased remarkably with increasing film thickness, tending to a constant value ($9 \times 10^{-2} \mu m$) for films thicker than about $1.6 \mu m$. We removed a worn silica film $0.6 \mu m$ thick from the substrate with hydrofluoric acid and found on the PMMA substrate surface tracks made by moving grains of kaolin powder through abrasive wear. This suggests that the abrasive wear action of the kaolin–water suspension causes a large shearing force between the silica film and the substrate when the film thickness is thinner ($0.6 \mu m$), resulting in the film cleaving from the substrate. A large scatter in the wear data for the film $0.6 \mu m$ thick is due to the almost complete removal of the film on abrasive wearing.

The thicker films ($1.6 \mu m$) experience a decreased shearing force acting at the film–substrate interface during wear, causing no cleavage but a homogeneous layer-by-layer removal in abrasion. Thereafter SiO_2 films of thickness greater than $2 \mu m$ were used for experiments.
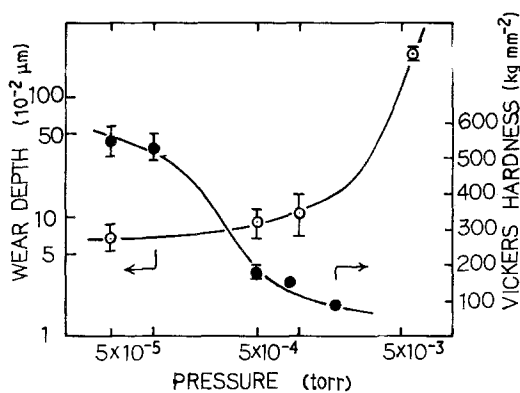
Figure 3 Relationships between ○ wear depth and ● film hardness with pressure.

3.2. Deposition conditions and abrasive wear

3.2.1. Effect of pressure

Wear properties of the evaporated SiO_2 films were investigated in relation to film hardness and pressure during film deposition. We prepared the films at pressures ranging from 5×10^{-5} to 5×10^{-3} torr with a deposition rate of $1 \mu m \, min^{-1}$, the film thickness being $2.5 \mu m$ for all specimens. Fig. 3 shows the films to be more susceptible to abrasive wear at higher pressure, and in particular a film made at 6×10^{-3} torr was almost detached from the substrate during wear because of weak adherence between the film and the PMMA substrate.

Films made by resistance heating evaporation at pressures from 5×10^{-5} to 1×10^{-3} torr gave Vickers hardness values of 550 to $150 \, kg \, mm^{-2}$. If we estimate the porosity of the film from its measured density, a value of 30% is expected for a film made at 1×10^{-3} torr pressure [2]. Thus a film prepared at higher pressure is rather loose in its structure.

Since the Vickers hardness is proportional to plastic yield stress Y of the material [4], a large variation in abrasive wear should be expected if plastic deformation occurs in wearing at the SiO_2 film surface. However, in fact a large variation in abrasive wear depth was not seen ($\sim 3 \times 10^{-2} \mu m$) in spite of a large change in film hardness, as shown in Fig. 3. From this we deduce that plastic deformation takes no part in the wearing process. Rather, chemical properties are presumably dominant in the SiO_2 wear process, i.e. the mechanical removal by kaolin particles of a hydrolysed surface layer of SiO_2 film occurs, hydrolysation being caused by water in the abrasive slurry.

Fig. 4 shows worn surfaces of silica films made at different pressures. The arrow shows the direction of abrasive wear. For the film made at a pressure of 5×10^{-4} torr one can see many linear abrasive wear tracks parallel to the direction of abrasion, which are considered to be produced by sliding or rolling kaolin particles suspended in the felt tool. These tracks were also found on worn films made at 1×10^{-3} torr. The appearance of these tracks indicates a continuous local removal of material without extended fissues along the direction of movement of the particles.

On the other hand, for the film made at 5×10^{-5} torr pressure we see along the abrasion direction not continuous wear tracks but discontinuously dotted micro-cracks. This means that when the film is too hard, shearing forces caused by sliding or rolling abrasive grains produce these discrete fissures.

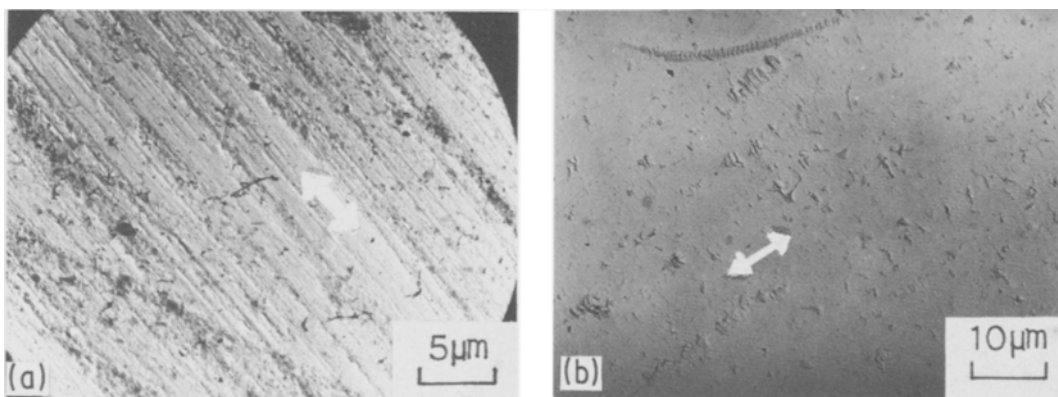These differences in appearance are not seen

Figure 4 Worn silica film surfaces: (a) 5×10^{-4} torr; (b) 5×10^{-5} torr.
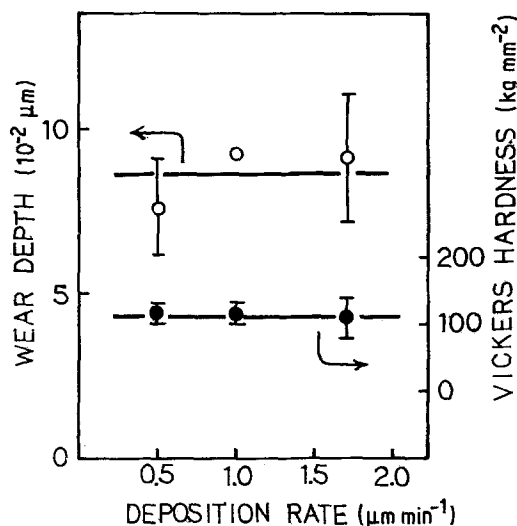
Figure 5 o Wear depth and ● Vickers hardness of silica films versus deposition rate.

distinctly in the abrasive wear shown in Fig. 3; this may be due to the averaging effect of our method of wear measurement using X-ray fluorescence.

3.2.2. Effect of deposition rate and source—substrate distance

Fig. 5 shows the dependence of abrasive wear on deposition rate of films made at 1×10^{-3} torr pressure. The film hardness was about $120 \, kgmm^{-2}$, the film density being $1.67 \, g \, cm^{-3}$, which was independent of the deposition rate. The abrasive
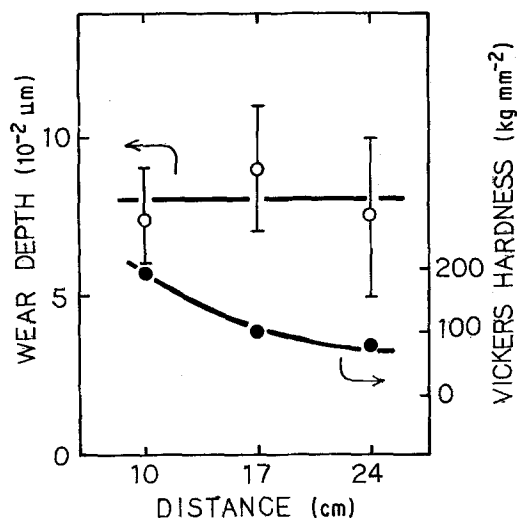

Figure 6 o Wear depth and ● Vickers hardness of silica films versus source—substrate distance. Pressure 500 g cm^{-2}; 2000 runs.

wear depth was also shown to be constant for these different rates.

We next varied the source—substrate distance at a pressure of 1×10^{-3} torr. The results of tests of abrasive wear and hardness are shown in Fig. 6. The amount of wear was constant irrespective of film hardness varying from 200 to $80 \, kg \, mm^{-2}$ for distances from 10 to 24 cm. The change in film hardness is considered to be due to the fact that a larger distance gives a higher probability of collisions between evaporated SiO_2 molecules and residual gases, resulting in the production of a loose structure and lower film density.

Summarizing the results in Sections 3.2.1 and 3.2.2, we consider that the abrasive wear of deposited SiO_2 films is mainly a mechanico-chemical phenomenon between kaolin particles sliding or rolling under pressure and the SiO_2 film in local contact with the particles, and that the structure and hardness of the film are not dominant factors, at least in the pressure range 5×10^{-5} to 1×10^{-3} torr. However, when the films are made at a higher pressure (1×10^{-3} torr) and the structure becomes looser, giving higher porosity and weak adherence to the PMMA substrate, the film is removed by the abrasive wearing action of the grains. This view of wear differs from normal theory and results based on material hardness [1, 5].

3.3. Wear characteristics

Abrasive wear characteristics of deposited SiO_2 films were investigated using the abrader shown in Fig. 1 to obtain much information on the mechanism of wear of SiO_2 by kaolin particles. The films were made at a pressure of 5×10^{-4} torr with a deposition rate of $1 \, \mu m \, min^{-1}$, the film thickness being fixed at $3.2 \pm 0.5 \, \mu m$ throughout the experiments. The wear conditions were varied in terms of pressure and wearing time. Fig. 7 indicates that the wear depth at a pressure of $500 \, g \, cm^{-2}$ is proportional to the number of runs of the felt abrader containing kaolin—water slurry. This means that a homogeneous abrasive wear occurs at the extreme surface of the film during abrasion. The effect of wear pressure on abrasive wear depth for 2000 runs of the abrader is given in Fig. 8. Obviously a linear relationship between wear depth and pressure is again seen in the range 50 to $500 \, g \, cm^{-2}$.

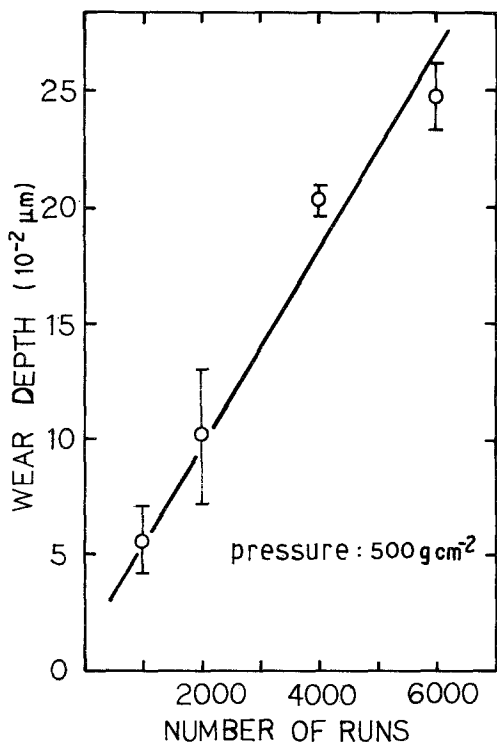We measured the profiles of worn surfaces in the direction perpendicular to that of the abrasive

Figure 7 Relation between wear depth and number of runs of abrasion.

Figure 8 Relation between wear depth and pressure of abrasion. 2000 runs.

wear using a Talystep profile meter as shown in Fig. 9. It was found that the local flatness of the SiO_2 films was diminished by the occurrence of fine and deep grooves with increasing abrasive wear pressure. This suggests that as the pressure increases, a local concentration of wear forces caused by abrasive powder particles occurs in the film, producing microcracks in the film during the sliding or rolling of the particles.

These wear characteristics of vacuum-deposited SiO_2 films as a function of wear conditions are exactly similar to the case of oxide materials, e.g. glasses, strongly suggesting that the wear mechanism is very much similar to that of glass polishing. In fact the polishing of various glasses by CeO_2 powder shows the same linear relationships between glass weight loss and polishing time and pressure respectively [6, 7] as seen in the abrasive wear of SiO_2 films (Figs. 7 and 8). It is acknowledged that glass polishing consists of the mechanical and molecular removal of a hydrolysed silica surface layer by polishing particles. Hydrolyzation caused by the polishing agent, water, [7, 8] favours the removal of material.

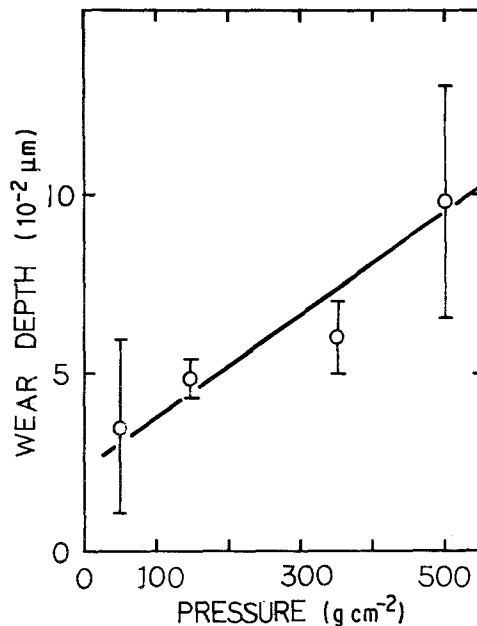Vacuum-deposited SiO_2 films are considered to be largely similar in the nature of their chemical bonding to oxide glasses, although the former are much looser in structure than glass. In the present abrasive wear experiments kaolin was used as an oxide mineral in a water slurry. Thus the hydrolysation of SiO_2 may play a basic role in the abrasive wear of deposited films; kaolin grains may mechanically remove the hydrolyzed SiO_2 surface layer by successively breaking Si–O bonds. This wear mechanism also explains the result that abrasive wear is almost independent of film microhardness (Fig. 3). It has been claimed that abrasive wear depends directly on the hardness and chemical bond strength of the material [9], but as has already been seen, this does not always hold for the abrasive wear of thick SiO_2 films when abraded with oxide minerals (such as kaolin) suspended in water.

4. Conclusions

Vacuum-deposited thick silica films on PMMA substrates have been worn unidirectionally with kaolin powder–water slurry. When the abrasive wear was measured as a function of film deposition conditions and film hardness, the wear depth of silica films was nearly constant over the pressure range from 5×10^{-5} to 5×10^{-3} torr, irrespective of large variations of film hardness ($100–550 \, kg \, mm^{-2}$). The film hardness had no effect on abrasive wear. Above 6×10^{-3} torr

1μm I

_____ (a)

⊢—⊣
1mm

1μm I

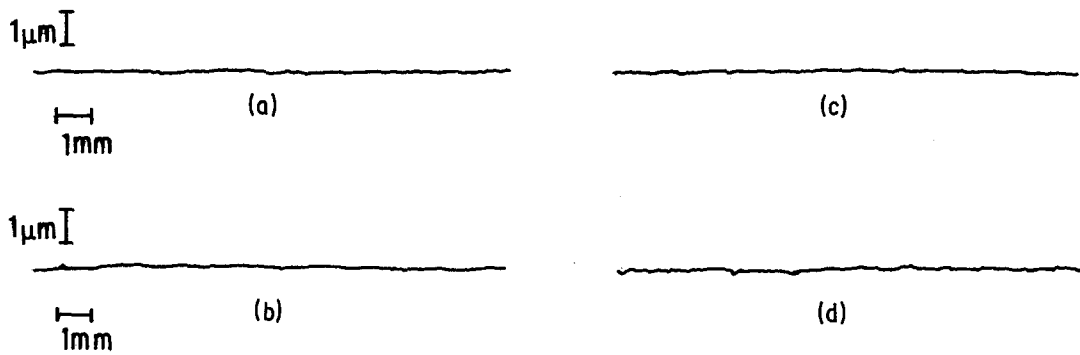_____ (b)

⊢—⊣
1mm

_____ (c)

_____ (d)

Figure 9 Profiles of worn silica film surface for different abrasion pressures: (a) 50 g cm^{-2}; (b) 150 g cm^{-2}; (c) 350 g cm^{-2}; (d) 500 g cm^{-2}.

pressure, the films were detached during wearing; the adhesive force between the film and the substrate was apparently responsible for abrasive wear.

Wear characteristics and the worn surface profile show strong evidence that abrasive wear consists of mechanical and molecular removal at local contacts by kaolin particles, with the SiO$_2$ film surface hydrolysed by the action of water in the kaolin—water slurry. This is very similar to the case of glass polishing by CeO$_2$ powder suspended in water.

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