Investigation of sliding wear surfaces in alumina using transmission electron microscopy

S. Chaiwan, M. Hoffman, P. Munroe*

School of Materials Science and Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

Received 7 July 2006; accepted 6 November 2006
Available online 22 January 2007

Abstract

In this study, the subsurface microstructure of alumina wear surfaces and the microstructure of agglomerated debris generated from unlubricated sliding wear at room temperature have been investigated through transmission electron microscopy (TEM). Specimens were thinned through the use of a focused ion beam miller (FIB). TEM studies, including analysis of electron diffraction patterns from the agglomerated region of the specimen, revealed the presence of an aggregate of nano crystalline particles embedded in an amorphous phase, together with some larger alumina particles. These larger alumina particles appear at the base of pits in the alumina surface, whereas the finer material appears at the contact surface. The agglomerated debris was readily distinguished from the alumina substrate, which contained localised dislocation damage and microcracking. It is proposed that the wear process involves the removal of ‘large’ alumina particles from the surface by a combination of trans- and intergranular microcracking. These particles are then ground into very fine, nanometer-sized particles that react on the surface with moisture in the air to form an amorphous hydroxide film. These are then compacted to form a nanocrystalline structure within an amorphous matrix that may also be viewed as a grain boundary phase.

Keywords: Mild wear; Alumina; Debris agglomeration; FIB; TEM

1. Introduction

The wear of alumina-based ceramics is recognised to be a multistage process, that is strongly affected by the formation of tribofilms during abrasion [1–3]. The structure of these films is, however, poorly understood. Initially, during sliding, particles are fractured from the material surface. These particles may then be ground into fine wear debris that undergoes a compaction process to form a tribofilm on the surface. Ceramic wear surfaces may range from rough following surface fracture to highly polished with a surface tribofilm [1,4].

A number of studies have investigated the factors associated with surface fracture including indentation and scratch testing [5]. Additionally, detailed investigations of surface microcrack formation during sliding have found that microcracks form more readily as the grain size increases [6,7]. During wear, microcracking is initiated by the pileup of dislocations at grain boundaries resulting in a microcrack at the boundary between adjacent grains. This process may be cumulative, with a number of wear passes necessary before microcracks form in a fatigue-type process [7,8]. Additionally, microcrack formation has been found to occur more readily as the grain size increased. Griffith fracture mechanics, utilising the grain size as the critical defect length, has been used to model the effect of grain size upon microcrack formation [7].

Ultimately, microcracking leads to particles being removed onto the wear surface in the form of debris. The grinding of these surface particles into finer wear debris precipitates the formation of a tribofilm on the wear surface. At elevated temperatures up to 900 °C, it has been found that the film is formed by resintering of the fine alumina particles under pressure exerted by the wear partner [3]. This resintered material has been found to fill pits in the wear surface. Combined with the smoothing of alumina, this results in a smooth polished surface. At 900 °C, the hardness of this sintered tribofilm increases to 22 GPa at high contact pressure, but decreases
significantly with test temperature to a median value of \( \sim 3 \) GPa at 200 °C.

Tribofilms also form at room temperature in an ambient environment where sintering is not possible, but where there is H\(_2\)O in the atmosphere [4,9–14]. This can also lead to a smooth polished surface [3]. Alumina tribofilms range from localised islands, which fill surface pits, to a more uniform 1–2 \( \mu \)m thick film that covers the surface and the type of film significantly affects friction behaviour [15]. A recent study, in which a wear test was undertaken at decreasing pressure with sliding distance, found initially, when the surface was purely polished alumina, that the friction coefficient was quite high [15]. However, as sliding continued and pressure decreased, a surface film formed that completely covered the surface and the friction coefficient fell. Further sliding, combined with decreasing pressure, re-exposed \( \sim 11\% \) of the area of the alumina on the sliding surface (with tribofilm material in surface pits) and the friction coefficient rose again. This shows that the tribofilm has a lower friction coefficient than pure alumina, as has been proposed by others [4]. Subsurface cross-sectioning revealed that the tribofilm layer became more compacted as sliding progressed.

A number of studies have considered the chemical and microstructural nature of these tribofilms formed during sliding wear of alumina [4,10,11,15]. Utilising a wide range of techniques including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), X-ray energy dispersive spectroscopy (EDS), secondary ion mass spectroscopy (SIMS) and Fourier transform infrared spectroscopy (FTIR), theses studies have revealed that an aluminium hydroxide compound is present, which is formed by the reaction of fine alumina wear debris with moisture in the surrounding atmosphere. This film is possibly amorphous. Nanoindentation of the film has shown it to be quite soft [10], unlike the analogous film formed at high temperature. It has also been hypothesised that fine alumina particles may be present in the film [4], although these were not been imaged nor unambiguously identified. However, a recent relevant transmission electron microscope (TEM) investigation of wear debris formed during sliding wear of silicon nitride ceramic revealed that the debris particles were, in fact, compacted fine ceramic particles [13].

In summary, the exact nature and structure of the tribofilm developed during wear of alumina in a humid room temperature ambient environment and its formation process is not fully understood. In this present work, focused ion beam (FIB) milling was used to prepare in situ TEM samples of the cross-section of a wear surface in alumina formed in room temperature ambient conditions. These enabled identification of the microstructure of the tribofilm formed. Furthermore, imaging of a complete cross-section of the alumina substrate and the interfacial region between the substrate and tribofilm elucidates the process of alumina wear and subsequent tribofilm formation.

### 2. Experimental method

#### 2.1. Material processing and wear testing

Alumina pin and disc wear testing samples were prepared from high-density \( \alpha \)-alumina (supplied by Taylor Advanced Ceramics, Mortdale, Australia) with 4.2 \( \mu \)m average grain size (solid state sintered, 99% purity). This material was initially near net-shape sintered in the form of a disc of 50 mm diameter and 5 mm thickness and a pin 25 mm long pin with a 6 mm diameter. These were then annealed at 1400 °C for 10 h to achieve the required grain size.

A hemispherical head was then ground on the end of the pin followed by polishing down to a 1 \( \mu \)m finish with diamond paste. The surface of the disc was ground flat and polished similarly. After cleaning with acetone in an ultrasonic bath, a surface roughness of 0.33 \( \mu \)m was measured on both wear pieces using a surface profilometer.

A self-mated alumina sliding wear test was then undertaken using a CSEM pin-on-disc tribometer for the purpose of preparing a wear surface possessing a well-formed tribological surface layer. The choice of testing conditions was based upon the results of a previous study [15], namely, a normal load of 2 N at a constant sliding velocity of 5 cm/s. Testing was in ambient conditions of 64% relative humidity and 24 °C and undertaken for a 3 km uninterrupted sliding distance. This process results in the formation of circular wear scar on the pin that increases in diameter with increasing sliding distance, resulting in a corresponding decrease in contact pressure. At the completion of the current test the contact pressure was 3.75 \( \pm \) 0.05 MPa, as determined from the normal load and wear scar area. Wear data, in terms of the scar diameter and wear rate were calculated for a range of distances up to 5 km (Table 1).

#### 2.2. TEM sample preparation

After the scar was prepared, as described above, a \( \sim 30 \) nm thick gold coating was sputtered onto the surface of the pin. The purpose of this was to assist in the preservation of the original wear-scar surface topography. It has been shown that such gold layers are highly effective in preserving the surface structure of specimens during FIB-based preparation methods [16].

| Wear distance (m) | Scar diameter (mm) | Wear rate \((\text{mm}^3/\text{km})\) | Depth change \((\mu\text{m}/\text{km})\) |
|------------------|-------------------|-------------------------------|--------------------------|
| 10               | 0.452             | \(1.9 \times 10^{-2}\)       | >110                     |
| 400              | 0.635             | \(1.1 \times 10^{-4}\)       | >0.35                    |
| 2.4 km           | 0.667             | \(8.3 \times 10^{-5}\)       | 0.24                     |
| 5.0 km           | 0.676             | \(1.5 \times 10^{-4}\)       | 0.42                     |
A thin cross-section was then taken of the pin head including the wear scar as illustrated in Fig. 1. The section was prepared such that its width direction was perpendicular to the sliding direction. Firstly, two vertical slices were made using a diamond wafering saw resulting in a \(\frac{1}{2}\) mm thick section. This section was removed from the pin, mounted on a Pyrex stub using resin and thinned down using a polisher (South Bay Technology Tripod Polisher Model 590P). This was undertaken using SiC grit papers (mesh number 600, 800, 1200 and 2400, successively) and reduced the sample thickness down to \(\frac{1}{2}20–50\) \(\mu\)m. Polishing with the fine grit papers also served to remove the damage caused by the abrasive diamond-cutting process. The mechanically thinned sample was detached from the polishing holder using acetone, was then cut using a razor blade and glued onto a half-circle copper grid using an M-bond 610 adhesive (Micro-Measurements Group, USA) as illustrated in Fig. 2. After curing in a 60\(^\circ\)C oven for 30 min, the piece was coated with a protective layer of vaporised gold in a sputter vacuum coater. The thickness of the coating was \(\approx 4\) nm.

An electron transparent sample (\(\approx 200\) nm thick), which was tapered towards its edge, was then prepared using a FIB [17]. Here, the prepared thin sample was vertically mounted in the FIB specimen chamber. As shown in Fig. 3, a 1 \(\mu\)m thick layer of platinum was deposited in the FIB, prior to ion milling, to preserve the surface of interest near its edge from unwanted erosion during the FIB milling process. A series of ion beam currents, in the range of 6700–350 pA, was used to selectively sputter the material under the focused beam (as described in detail elsewhere [15]). A trench size of approximately 5 \(\mu\)m wide by 5 \(\mu\)m depth was made leaving an electron transparent section \(\approx 200\) nm in thickness. The specimen was then examined in a Philips CM200 TEM to which an EDAX EDS detector was interfaced. It should be noted that the energetic gallium ion beam in the FIB may lead to the introduction of some artefacts during the preparation of electron transparent membranes [18]. However, there is insufficient heat generated to induce localised crystallization when, during the preparation of TEM cross-sections, especially as the beam is maintained parallel to the thinned section [19]. It has also been shown that localised redeposition effects have minimal effects on the observed microstructures in ceramic materials prepared via FIB milling [18].

3. Results

Fig. 4 shows two bright field TEM images prepared from the same wear surface. These specimens were located approximately 150 \(\mu\)m apart, however, they show very different surface debris and substrate characteristics. Considering Fig. 4(a), the wear surface is the top right-hand side of the image, specifically the regions, labelled A and B. Above that is the platinum protective layer (the dark region marked X). A number of debris particles formed by the mechanical thinning and polishing during the TEM preparation process are seen to be adhered to the platinum layer. The wear surface consists of two distinct regions. Firstly, an alumina grain can be seen on one side (labelled A). This grain exhibits a significant density of dislocations. Secondly, to the right of this grain, is a pit in the alumina surface which has been filled by wear debris (B). This debris layer consists of compacted particles, shown by electron diffraction studies to be alumina, ranging in size from coarse particles (100–500 \(\mathrm{nm}\) in diameter) down to very fine particles (unresolvable in this image) and is fractured into various pieces. The relatively large (100–500 \(\mathrm{nm}\) diameter) abrasive particles in region B also appear to contain a high density of dislocations. The
difference in sizes of wear particles suggests intergranular and/or transgranular abrasion took place during the wear process. Size reduction is also evident as the smaller particles contain dislocations, that resulted from high stress during a three-body wear process. The very fine debris is presumably formed by grinding of larger alumina particles during the wear process. To the bottom left of the image, and below the wear surface is a large alumina grain (labelled C) which shows no significant density of dislocations or other damage.

Fig. 4(b) shows another section of the same wear surface structure, but as noted above ~150 μm away from the region shown in Fig. 4(a). In this image, the region labelled “D” represents debris agglomeration and regions “C” and “X” represent the substrate and platinum deposition, respectively. However, in this micrograph there are no traces of coarse wear debris deposited underneath the debris agglomeration. The thickness of the agglomeration ranges from 1–2 μm and is noted to be well separated from its substrate.

Fig. 5 is a magnified image of the debris region “D” from Fig. 4(b) and shows that the debris agglomeration, marked A, exhibits a fine mottled structure. The region marked B shows an alumina grain below the damaged region. An
electron diffraction pattern from the debris agglomeration region is presented in Fig. 6. The pattern consists of a ring pattern. The diameters of these rings are consistent with the presence of $\alpha$-alumina, that is a hexagonal phase with lattice parameters of $a = 0.475 \text{ nm}$ and $c = 1.299 \text{ nm}$. These ring patterns indicate the presence of a very fine-grained phase, such that a large number of grains are contributing to the pattern. There is also significant diffuse contrast in these diffraction patterns which is suggestive of the presence of an amorphous phase. It is not possible in this case to show unambiguously the presence of an amorphous phase, but the diffuse contrast in Fig. 6 is suggestive of its presence. The overall diffraction pattern from this region of debris agglomeration suggests, therefore, that the structure contains a mixture of amorphous and very fine, crystalline phases.

Fig. 7 shows bright and dark field images of the debris agglomeration, that is the region labelled as region “D” in Fig. 4(b). The dark field image was obtained by placing the objective aperture around one of the discrete reflections in the rings in the selected area diffraction pattern obtained from this region (Fig. 6). A number of particles are illuminated in the dark field image, which are typically 5–30 nm in diameter and presumably crystalline in nature. It should also be noted that only a small fraction of these particles will be illuminated in such a dark field image, and therefore the density of such particles in this region will be overall significantly higher. The dark area that encloses the agglomerated region, which can be seen in both the bright and dark field images, is the deposited platinum.

A region of the alumina wear surface substrate is shown in the bright field TEM image shown in Fig. 8, that is the grain marked “D” in Fig. 4(b). The polycrystalline alumina substrate contains both microcracks and dislocations. Dislocations appear immediately underneath the top of the substrate and the microcracks appear beneath the dislocations. However, both types of damage terminate at an adjacent grain boundary. Additionally, slip planes and intergranular and transgranular cracks were observed in some areas in other TEM samples. However, all observed damage and deformation occurs within 1–2 $\mu\text{m}$ beneath the interface between the substrate and wear debris or the alumina wear surface.

Microchemical analysis of both the region of debris agglomeration and the substrate was performed using EDS. However, this technique cannot detect hydrogen, so unambiguous identification of aluminium hydroxide via this technique is not possible. The spectrum shown in Fig. 9(a) is taken from the substrate (region A in Fig. 5). Significant concentrations of both silicon and calcium, in addition to aluminium and oxygen, are evident in this spectrum. These elements are added to improve sintering. In contrast, the spectrum taken from the debris agglomeration layer (Fig. 9(b)) (region B in Fig. 5) indicates that this region is much leaner in both calcium and silicon, and consists primarily of oxygen and aluminium. As described earlier, this debris layer consists of fine, $\sim$10–30 nm diameter, crystalline particles in an amorphous matrix. The spatial resolution of EDS in this instance, where such fine particles are embedded in a TEM specimen, typically 200 nm in thickness, means
that the chemical compositions of the matrix phase and the particles embedded in it cannot be unambiguously distinguished.

4. Discussion

TEM data from cross-sectioned wear surfaces present a sequence of events and features which assist in elucidating the mechanisms of wear within the “mild” wear regime. As shown in Fig. 4, there are two structural characteristics of debris agglomeration, one with a mixture of both coarse and fine debris particles (Fig. 4(a)) and the other with purely fine debris (Fig. 4(b)). Although both TEM specimens were taken from the same wear surface (although about 150 μm apart on the same surface), it is clear that during the wear process both macro- and microabrasion processes, which represent fracture and polishing actions, respectively, took place.

Some coarse particles also are present at the top part of the debris layer, although none are exposed to the actual wear surface. This suggests that macroabrasion, as well as size reduction through microabrasion, occurred during the running-in stage. As the wear process progressed macroabrasion decreased until only microabrasion took place. During the microabrasion stage, the alumina surface becomes polished and the wear rate was minimal [15]. A dynamic process causes the fine wear debris to continuously wear away and to be re-deposited in cavities in the wear track. This means that the coarse debris appears to be deposited more deeply and agglomerations of fine debris are laid on top.

A detailed investigation of the coarse debris particles embedded in the TEM specimen shown in Fig. 4(a) showed dislocations within them. As described earlier, the abrasion process caused the wear particles to deform plastically. Fatigue from the rolling slide and stress concentration...
from the abrasion caused dislocations to move and eventually caused fracture of the particles. The deposition layer, or the so-called tribofilm, appears to some degree to be well separated from its substrate. From Fig. 5 it is seen that the lower edge of the tribofilm is smooth and its shape profile corresponds to the substrate. The exact reason for this separation is unclear. However, similar observations on alumina wear surfaces indicate that it was not caused by the sample preparation process used in this study.

The electron diffraction pattern taken from the region of debris agglomeration (Fig. 6) shows that the presence of both discrete reflections, which can be used to excite contrast from fine, crystalline particles in this region, and broader rings, indicative of amorphous material. This suggests that this phase consists of nanocrystalline particles, a few tens of nanometres in diameter embedded in an amorphous matrix. The small size of these particles, and the fact that they are much smaller than the TEM specimen thickness, and therefore entirely embedded in the matrix, mean that detailed and unambiguous identification of these particles is not possible. A number of authors have stated that alumina tribofilms are amorphous in nature, and contain aluminium hydroxide in various forms [10,11], which is partially consistent with the present observations.

The TEM observations and diffraction analysis show that the film consists mainly of crystalline nanoparticles, this is not consistent with observations of mainly amorphous aluminium hydroxide in the films [11]. In a related study of tribochemical wear of Si3N4 in water [14], it was shown that the wear process initiated with the formation of Si3N4 wear particles which were finely ground and then reacted with the surrounding water to form silica films on the surface of the particles. As the wear process continued, these particles reacted completely to form a silica tribofilm.

It is proposed, therefore, that in the present case of the wear of alumina in air, fine alumina wear particles react with water in the air to form a hydroxide film on the surface of the particle. This hydroxide film becomes a part of the grain boundary phase between the nanoparticles. One would normally expect that a very fine-grained material would demonstrate high hardness, consistent with Hall–Petch type considerations. However, the presence of a relatively large volume fraction of low-hardness amorphous material between the grains serves to reduce hardness. This would also be consistent with the relatively low hardness of the tribofilm observed elsewhere [10].

Of note also is the fact that the Si and Ca peaks in the EDS spectra of the substrate in Fig. 9(a) are larger than those of the debris agglomeration layer (Fig. 9(b)). Si and Ca are sintering additives which have been shown to segregate to the grain boundaries in alumina. It would appear also that these elements are not involved in reactions which are associated with formation of the tribofilm.

Previous work [15] has shown that the wear surface of polycrystalline alumina, after a long (3 km) run-in period in the mild wear mode, had a coverage of 11% polished alumina with the remainder being debris agglomeration. The proportion of polished wear surface depended upon the sliding distance and contact load. Grain size and the amount of impurities in the alumina can also affect the
crack path occurring during the abrasion process [5]. A random crystallographic orientation of the alumina was also found to prohibit deformation processes such as twinning at the wear surface [20]. Within the mild wear regime, a comparison between nominal loads of 9.8 N used by Fischer et al. [9] and the 2 N load used in the previous work [15] showed that the quality of the visible polished wear surface varies depending upon contact load.

With a higher load the rate of material removal is proportionally higher. Dislocations caused by the high contact stress exerted by hard wear particles can alter the mode of fracture behaviour from intergranular to transgranular. Fig. 4 supports the description where the profile of the wear substrate shows intergranular fracture. Although the wear surface was subsequently deteriorated by intergranular fracture, dislocations were formed during the wear process (Fig. 8). These defects form in addition to the low density of crystalline defects present prior to the commencement of wear testing. These dislocations may act to induce a transgranular fracture mode. Fig. 8 also shows that the transgranular microcrack stopped at the grain boundary, as did the dislocations associated with its formation. The resultant debris particle would presumably be formed by a combination of transgranular fracture and intergranular fracture along the adjacent grain boundary. Relatively more transgranular fracture is required to form flat alumina surfaces which eventually results in a flat polished wear surface. In addition, the formation of a polished alumina surface was also suggested to be facilitated by a strong crystallographic orientation of some of the polycrystalline alumina grains [2,8] as the dislocation behaviour and subsequent microcrack formation is affected by crystallographic orientation.

5. Conclusions

In this study an analysis of subsurface deformation and the formation of tribofilms formed during the unlubricated sliding wear of alumina in air at room temperature was undertaken. This has revealed the following:

1. High stresses formed near the surface during sliding wear result in the formation of dislocations in the alumina which lead to the formation of intragranular microcracks. These microcracks lead to the removal of particles on the order of 500 nm in diameter from the surface which form wear debris.

2. These ‘large’ wear debris particles are ground during wear to form finer debris which becomes compacted as a tribolayer on the surface, especially in surface pits.

3. The surface tribolayer consists mainly of compacted alumina particles ranging in diameter from 5–30 to 100–500 nm within an amorphous matrix.

4. The larger alumina particles are found to sit in the base of surface pits and not close to the contacting surfaces.

5. Ca and Si impurities in the alumina appear in the tribolayer but at lower concentrations indicating that they are not a part of the amorphous matrix.

Acknowledgements

The authors would like to thank the Australian Research Council Grant and the Royal Thai Government Scholarship for financial support.

References

[1] Y. Wang, S.M. Hsu, Wear and wear transition mechanisms in ceramics, Wear 195 (1996) 112–122.
[2] W.M. Rainforth, The sliding wear of ceramics, Ceram. Int. 22 (1996) 365–372.
[3] K. Adachi, K. Kato, Formation of smooth wear surfaces on alumina ceramics by embedding and tribo-sintering of fine wear particles, Wear 245 (2000) 84–91.
[4] M.G. Gee, The formation of aluminium hydroxide in the sliding wear of alumina, Wear 153 (1992) 201–227.
[5] H.H.K. Xu, S. Jahanmir, Effect of grain size on scratch damage and hardness of alumina, J. Mater. Sci. Lett. 14 (1995) 736–739.
[6] H.H.K. Xu, S. Jahanmir, Y. Wang, Effect of grain size on scratch interactions and material removal in alumina, J. Am. Ceram. Soc. 78 (1995) 881–891.
[7] S.-J. Cho, B.J. Hockey, B.R. Lawn, S.J. Bennison, Grain-size and R-curve effects in the abrasive wear of alumina, J. Am. Ceram. Soc. 72 (1989) 1249–1252.
[8] J.D.O. Barceinas-Sánchez, W.M. Rainforth, On the role of plastic deformation during the mild wear of alumina, Acta Mater. 46 (1998) 6475–6483.
[9] T.E. Fischer, Z. Zhu, H. Kim, D.S. Shin, Genesis and role of wear debris in sliding wear of ceramics, Wear 245 (2000) 53–60.
[10] M.G. Gee, N.M. Jennett, High resolution characterization of tribochemical films on alumina, Wear 193 (1995) 135–145.
[11] R.S. Gates, S.M. Hsu, E.E. Klaus, Tribochemical mechanism of alumina with water, Trib. Trans. 32 (1989) 357–363.
[12] K. Cherif, B. Gueroult, M. Rigaud, Al2O3–ZrO2 debris life cycle during wear: effects of the third body on wear and friction, Wear 208 (1997) 161–168.
[13] J. Xu, K. Kato, The effect of water vapor on the agglomeration of wear particles of ceramics, Wear 202 (1997) 165–171.
[14] J. Xu, K. Kato, Formation of tribochemical layer of ceramics sliding in water and its role for low friction, Wear 245 (2000) 61–75.
[15] S. Chaiwan, M. Hoffman, P. Munroe, U. Stiefel, Investigation of sub-surface damage during sliding wear of alumina using focused ion-beam milling, Wear 252 (2002) 531–539.
[16] S. Rubanov, P.R. Munroe, The effect of the gold sputter coated films in minimising damage in FIB-produced TEM specimens, Mater. Lett. 57 (2003) 2238–2241.
[17] J.M. Cairney, P.R. Munroe, Preparation of transmission electron microscope specimens from FeAl and WC powders using focused-ion beam milling, Mater. Charact. 46 (2001) 297–304.
[18] J.M. Cairney, P.R. Munroe, Redeposition effects in transmission electron microscope specimens of FeAl-WC composites prepared using a focused ion beam miller, Micron 34 (2003) 97–107.
[19] S. Rubanov, P.R. Munroe, Investigation of the structure of damage layers in TEM samples prepared using a FIB, J. Mater. Sci. Lett. 20 (2001) 1181–1183.