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Al_2O_3 and Al_2O_3–TiN wear resistance in a simulated biological environment

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Alumina is widely used as a biomaterial because of its high biocompatibility and its good mechanical properties except toughness. In this study, a composite material Al_2O_3–TiN is considered as an alternative, the addition of TiN improving the mechanical properties of alumina. The wear behaviour of Al_2O_3 and Al_2O_3–TiN in aqueous solutions simulating living environments has been thus compared using a pin on disc wear-testing machine. The results show that the mechanisms of material removal during wear are different. For alumina, a mechanical wear mechanism is observed, reduced by the lubricating action of the wet media, and alumina–TiN is worn by a combination of tribochemical and abrasive effects.

1. Introduction

Ceramic materials, because of their superior mechanical and physical properties such as strength, hardness, chemical inertness and thermal shock resistance, are increasingly being considered for various tribological applications [1–3]. Sintered alumina with its unique combination of high hardness, corrosion resistance, thermal stability and low cost is the material widely adopted by industry. In particular, alumina has been increasingly retained as a biomaterial in prosthetic devices, such as replacement of acetubular cups and femoral spheres [4]. Because of its altogether satisfactory biocompatibility, alumina offers all the prerequisites for such applications. Moreover, its main advantages over other biomaterials such as metals and polymers in components of artificial joints are its low wear rates against itself [4] or against polyethylene, compared with metal/metal and polyethylene/metal combinations, and low concentration of inert wear particles in the surrounding tissue [5–8].

The main shortcoming of alumina, however, is its brittleness and its low toughness, which make it prone to catastrophic failure. It has been shown that brittle solids can be toughened by incorporating inclusions into them. In that way, alumina–TiN composites have been proposed for biomedical applications. The addition of TiN to alumina leads to an improvement in its strength and fracture toughness. Moreover, TiN itself is appreciated as a biomaterial. Because of a low coefficient of friction together with high hardness, it is often chosen as a surface coating to improve the tribological characteristics of materials. As a fine homogeneously dispersed phase within an Al_2O_3 matrix, TiN may be anticipated to be advantageous not only as a reinforcing agent but also to improve its surface properties.

In order to be considered as a potential biomaterial, such a new composite must demonstrate good biocompatibility and wear resistance in the corresponding environment. It is the purpose of this paper to report and discuss the results of preliminary experiments aimed at assessing the friction and wear behaviour of a particular Al_2O_3–TiN particulate composite in a medium mimicking a living environment, in comparison with that of a standard alumina used for hip prostheses. At the same time, the development of bone-cell colonies was also investigated on both types of surface [9].

2. Experimental procedure

2.1. Materials

Commercial alumina discs (Desmarquest) of the grade used for hip prostheses have been used to serve as a reference.

The dense Al_2O_3–TiN particulate composites were prepared by *in situ* reaction of $AlN + TiO_2$ powder compacts [10, 11]. The overall reaction can be written

$$3/2TiO_2 + AlN \rightarrow Al_2O_3 + 3/2TiN + 1/2N_2 \quad (1)$$

The final composition is 60% Al_2O_3 and 40% TiN by volume.

The properties of both materials are given in Table I. The composite has smaller grain sizes and improved mechanical properties [11, 12].

TABLE I Mechanical properties of alumina and alumina–TiN

	Alumina iso 6474	Alumina	Alumina–TiN	TiN
Density (g cm^{-3})	$\geqslant 3.90$	> 3.93	4.34	5.16
grain size (μm)	< 7	≈ 4	≈ 2	
Microhardness (Vickers)	2300	2300	2300	1800–2100
Breaking strength (three-point bend test) (MPa)	$\geqslant 400$	400	700	
Young's modulus (GPa)	380	310	410–420	480
Fracture toughness (MPa $m^{1/2}$)		4.6	5–6	

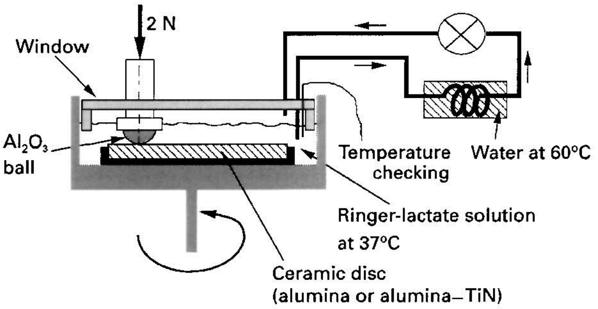

Figure 1 The apparatus of the wear test in pin on disc geometry in a corrosive medium at 37 °C.

After each test, microstructure modifications and wear volume in the track have been observed by scanning electron microscopy (SEM) coupled with energy dispersive analysis of X-rays (EDAX), electron probe microanalysis (EPMA) and X-ray photoelectron spectroscopy (XPS). Data on surface topography were obtained by means of scanning stylus profilometry (SSP). A specific software allows for high resolution, quantitative assessment of the wear volume from a statistically significant portion of the entire wear track.

2.2. Testing procedure

Tests were carried out on a pin on disc wear testing machine schematically shown in Fig. 1 and which had been modified to maintain both the samples and the corrosive medium at 37 °C. The latter medium is Ringer's solution, which contains in each 100 ml water: sodium chloride (0.6 g), potassium chloride (0.03 g), anhydrous calcium chloride (0.015 g) and sodium lactate (0.31 g). The experimental conditions were as follows.

(a) The disc material was either alumina or alumina–TiN with a diameter of 15 mm.

(b) The pin, for all tests, was a 1.58 mm diameter alumina ball (Saphirwerk Industrie-produkte AG Brügg-Switzerland).

(c) Tribological testing was performed under a normal contact load of 2 N. According to the Hertz relation, the initially applied contact pressure is roughly 25 N mm^{-2} and gradually decreases because of wear. The contact pressure applied on a hip prosthesis in the human body is approximately 20 N mm^{-2}.

(d) The surface had an average roughness of typically 0.02 μm.

(e) The speed of disc rotation was 60 r.p.m.

(f) The disc was mounted in a stainless steel cup containing Ringer's solution at 37 °C.

The friction coefficient was evaluated continuously during testing. Two types of tests have been performed: two continuous non-stop tests up to 172 800 ($\approx$ 4100 m) and 345 600 ($\approx$ 9–10 000 m) cycles as well as tests interrupted after every 72 000 cycles ($\approx$ 2500 m) for wear analysis.

3. Friction and wear behaviour in a corrosive environment

3.1. Friction coefficient evolution

In Fig. 2, the friction coefficient of specimens for the pin on disc arrangement is plotted versus the number of cycles during a continuous test up to 172 800 cycles. The evolution of the friction coefficients is representative of both types of experiment. The friction coefficient, whatever the combination (alumina/alumina or alumina/alumina–TiN) and test type, builds up rapidly until a "stationary" state is reached.

The friction coefficient of alumina is very stable all through the test and is around 0.30–0.35. This value compares well with data from other authors [1, 5, 13, 14]. Its favourable wear characteristics are generally attributed to adsorbed water on the surface. Alumina is a hydrophilic material with high wettability allowing very low friction with negligible wear [5].

In contrast, the friction behaviour of alumina–TiN is uneven. The friction coefficient varies back and forth between 0.4 and 0.5 as rather abrupt increases or decreases. In such cases, adhesive transfer and retransfer may occur at the interface between the alumina ball and alumina–TiN disc and have an effect on friction.

The comparison of friction data between both combinations suggests a distinct difference which must be related to the wear mechanism: to the way in which wear debris and transfer layer formation occur, presumably due to the presence of the TiN phase within the material.

3.2. Ball and wear track surfaces

In both tests, alumina balls are worn to some extent (Fig. 3). The track has a circular cross-section indicating a regular and progressive wear. The overall surface of the ball after the test on an alumina disc is smooth (Fig. 3a).

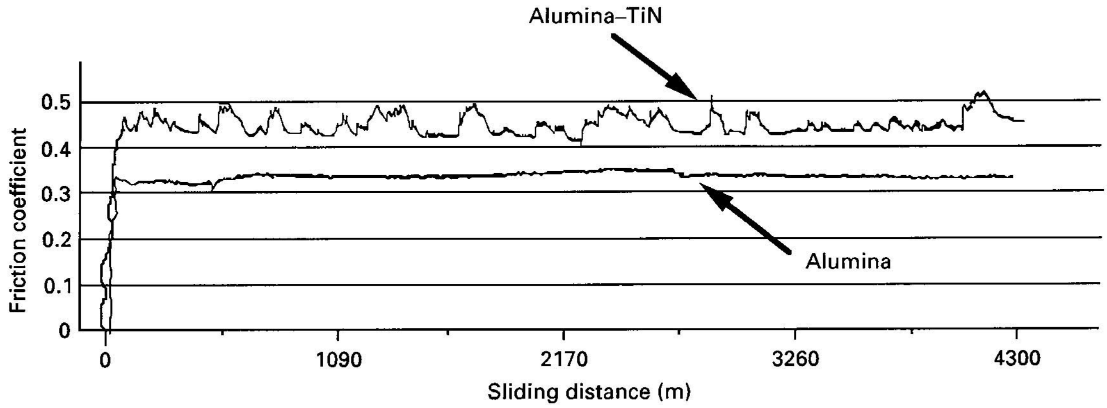

Figure 2 Friction coefficient evolution as a function of sliding distance during a continuous test up to 172–800 cycles.

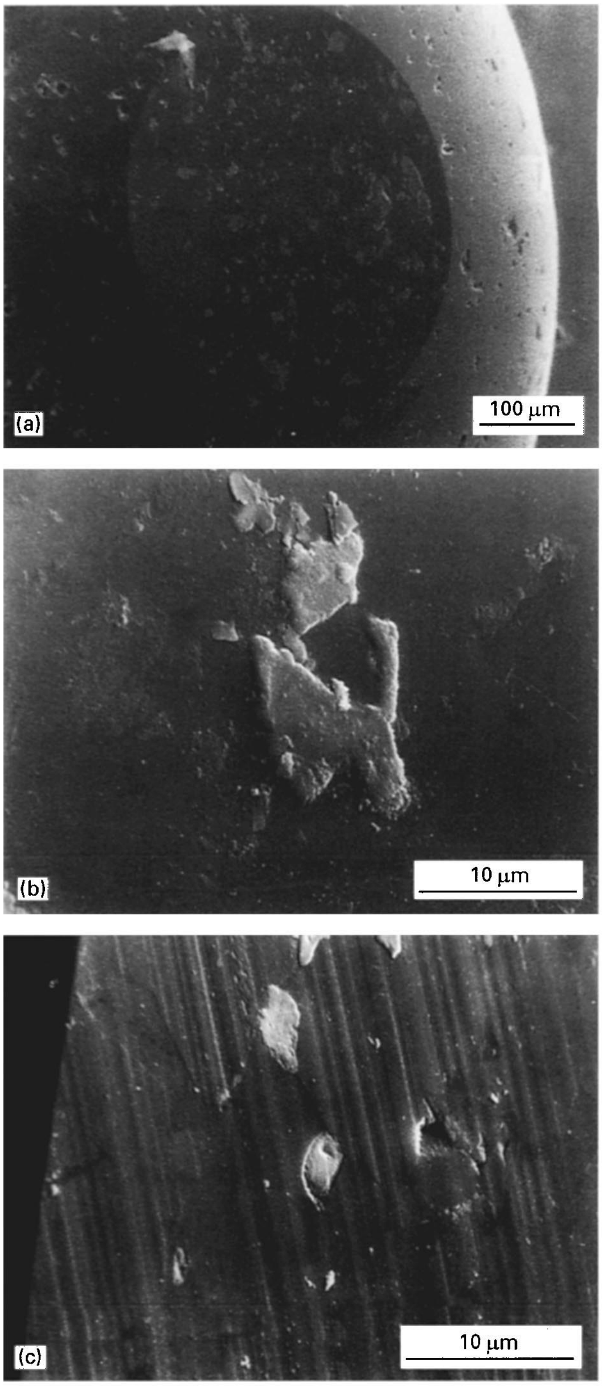

Figure 3 Alumina ball surface after wear tests (tilt 45 °): (a, b) on alumina disc (five runs of 72 000 cycles); (c) on alumina–TiN disc (345 600 cycles).

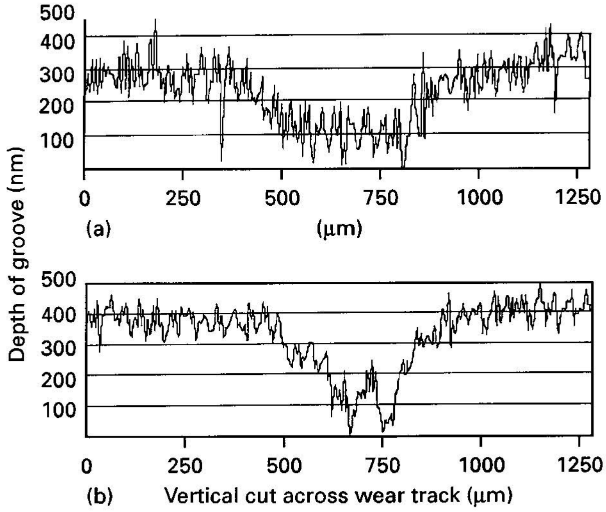

Figure 4 Topography of the wear track on (a) alumina and (b) alumina–TiN discs after wear tests of five runs of 72 000 cycles.

Against alumina–TiN discs, the alumina ball slide surface is crossed by scratches of micrometre size. This indicates a ploughing (microcutting) action during sliding (Fig. 3b). That implies that, akin to fine abrasive particles during surface polishing, hard wear particles from the alumina–TiN counter body groove the ball surface. Indeed EDAX analysis on chipped areas of the alumina ball surface show the presence of titanium. Thus, during the wear process, TiN particles are pulled out or evacuated and the resulting rough surface (remaining alumina grains on the disc surface) grooves the ball surface. Moreover, grooving cannot originate from the TiN phase as TiN is less hard than alumina.

Detailed information on the wear track topography of both types of test can be gained from SSP of the friction track. As can be seen in Fig. 4, in the case of alumina discs, the track cross-sections are roughly parabolic and continuous compared to those of the alumina–TiN discs, which consist of a set of grooves. The wear track of the alumina disc is broader and less deep than that of the alumina–TiN disc.

Wear volume, V, is plotted versus sliding distance in Fig. 5 for the discontinuous tests. Whatever the ceramic used, the wear volume is of the same order of magnitude and seems to follow a linear relationship

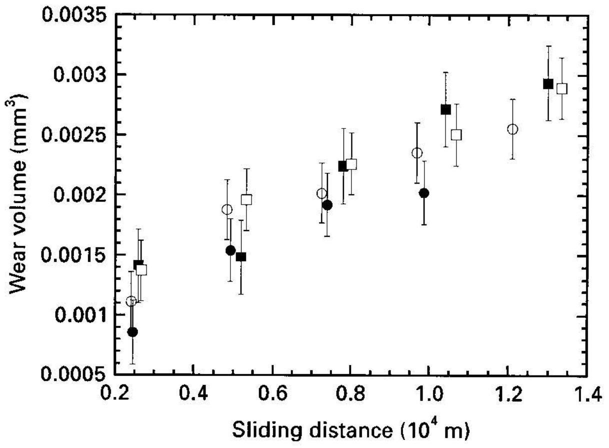

Figure 5 Wear volume as a function of sliding distance for all experiments. (●) Alumina 1, (■) alumina 2, (○) Alumina–TiN 1, (□) alumina–TiN 2.

with distance as expected from Achard's law. For continuous experiments, the final wear volume of alumina–TiN is smaller than that of alumina and similar to that for discontinuous tests.

The average wear factor, K, is defined as $K = (V/L_s)P$, where L_s is the sliding distance and P the load. The wear factors for alumina and alumina–TiN in our experimental conditions are in the range $1\text{–}2.5 \times 10^{-16}\,\mathrm{m^3\,N^{-1}\,m^{-1}}$ situated between mild wear (usually assumed below $10^{-18}\,\mathrm{m^3\,N^{-1}\,m^{-1}}$) and the severe wear regime of alumina ceramics above $10^{-14}\,\mathrm{m^3\,N^{-1}\,m^{-1}}$ [15].

3.3. Wear mechanisms

Fig. 6 shows surface damage features after a pin on disc test with alumina discs. Observation of the wear track reveals grain chipping to be the dominant mechanism of material removal for this alumina sample.

In the case of alumina–TiN discs, the mechanism is more complex, as can be seen in Fig. 7, where the unworn and worn areas are shown. In the composite microstructure, alumina grains are dark grey and TiN grains are white. It is clearly apparent that in the wear track the TiN grains are preferentially consumed. Further comparison (Fig. 8) of the microstructures outside and inside the wear track show that the track surface is smooth. Detailed analysis shows the presence of large white–grey parts. This suggests the formation of other titanium-based phases (possibly mixed titanium oxide or oxynitride) during the wear test. The formation of such mixed oxide phases would not be surprising, as smooth surfaces are generally indicative of a tribochemical wear process. Such surfaces have already been observed during wear tests with silicon nitride. They were claimed to result from the tribochemical reaction of silicon nitride with water [1, 3, 5, 16–18] to yield silica. This suggests that tribochemical reactions may also occur with TiN-based composites.

EPMA X-ray images of the wear track show that in these new phases titanium is also combined with oxygen and aluminium is always present simultaneously.

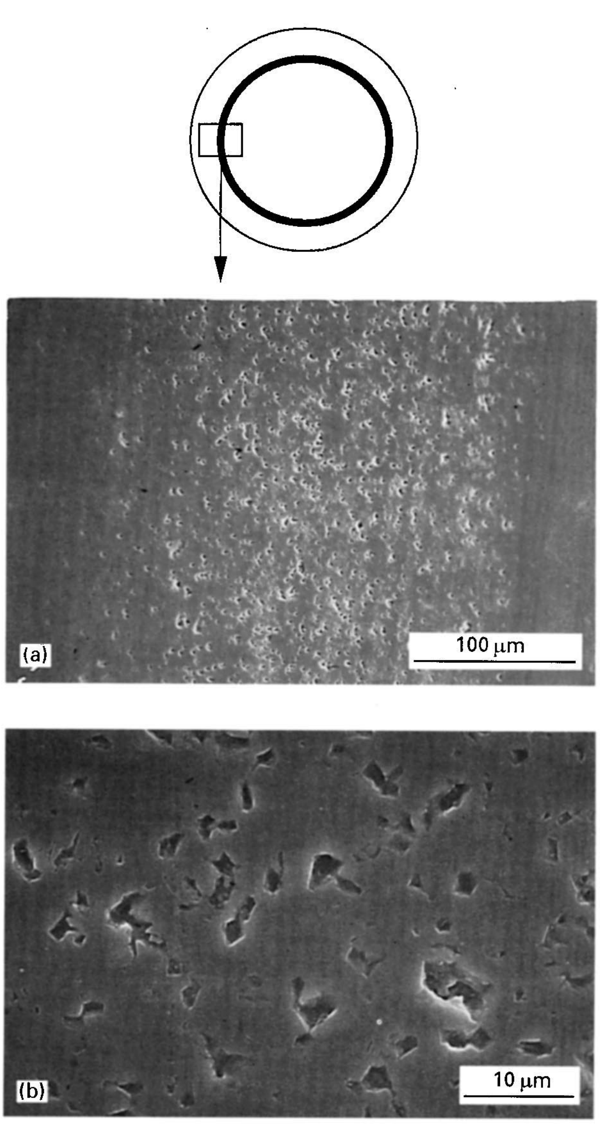

Figure 6 (a, b) Wear track on an alumina disc after continuous testing for about 345 600 cycles.

Direct quantitative analysis is difficult, considering that all elements are present. This may also be due to the fact that this phase corresponds to very small grains. However, as EPMA is sampling over a 1 μm thick surface layer, that may also mean that these phases are present as thin films at the very wear surface only. As quantitative and qualitative analysis techniques cannot prove unambiguously the oxidation of TiN, an alternative is to look for a modification of the valency of some titanium ions by XPS analysis. Further wear experiments have been performed to gain a very broad wear track and XPS analysis has been performed on the whole worn surface by shielding the unworn surface with a carbon coat. Before XPS analysis, the surfaces were cleaned up by ionic bombardment to evacuate a contamination layer of a few nanometres. The titanium XPS spectra of the worn alumina–TiN surface and the unworn surface are compared in Fig. 9. One type of titanium is characterized by XPS by two features in the spectra. In the case of the unworn surface, two features, marked 1 and 3 in the figure, are observed, associated with spin-orbits $2p_{3/2}$ and $2p_{5/2}$. On the worn surface, two more

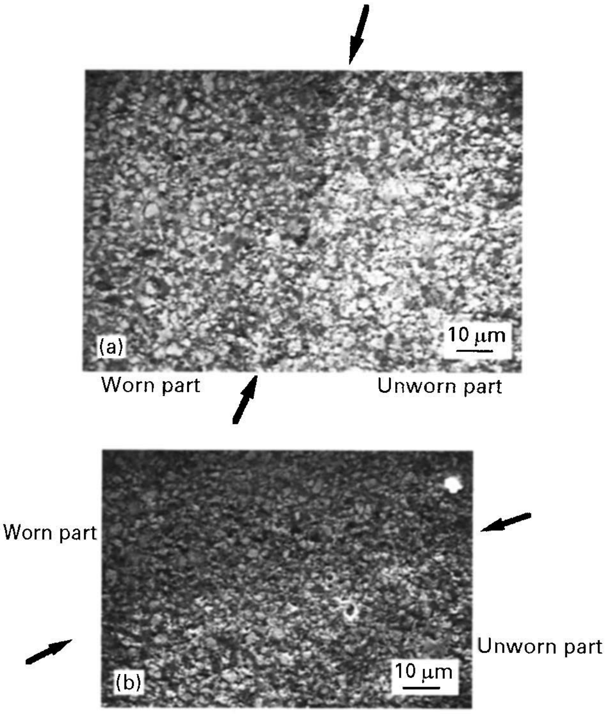

Figure 7 Microstructure along the wear track on the alumina–TiN disc surface after a wear test of five runs of 72 000 cycles.

features, marked 2 and 4, are present which indicate that two types of titanium are present on the worn surface: one which is the same as on the unworn surface and another which corresponds to an oxidized type of titanium. These experiments prove that TiN has chemically interacted with the surrounding medium.

3.4. Discussion

The usual wear mechanisms of ceramics are confirmed in the present experiments, in particular with alumina. Alumina is worn by chipping of entire grains. This is made possible by initiation of cracks at grain boundaries [19, 20]. Grain boundaries are the weakest link in the structure of the polycrystalline ceramic. First, small cracks are formed at grain boundaries, then coalescence of the cracks leads to local grain excavation and ultimately to massive destruction of the surface. Because of the brittleness of ceramics, various types of crack tend to develop by friction around the contact area, such as Hertzian, lateral, median and radial cracks [1]. Surface cracks may also be present from the very beginning, generated in the process of mechanical surface polishing.

Water has a lubricating action which is responsible for the low friction coefficient of alumina against alumina [5, 8, 13]. Water lubrication results in the formation of hydrided alumina surface films protecting the surface [1–3, 13, 14]. These surface layers reduce stress transfer across the wear interface and reduce the probability of grain chipping. Thus the tribochemical reactions induced by water in fact directly reduce the mechanical wear. However, it cannot be excluded that by penetrating into an existing crack, the aqueous medium also induces some stress-corrosion action at the crack tip, in addition to the effect of a shock wave propagation down to the tip [13, 19].

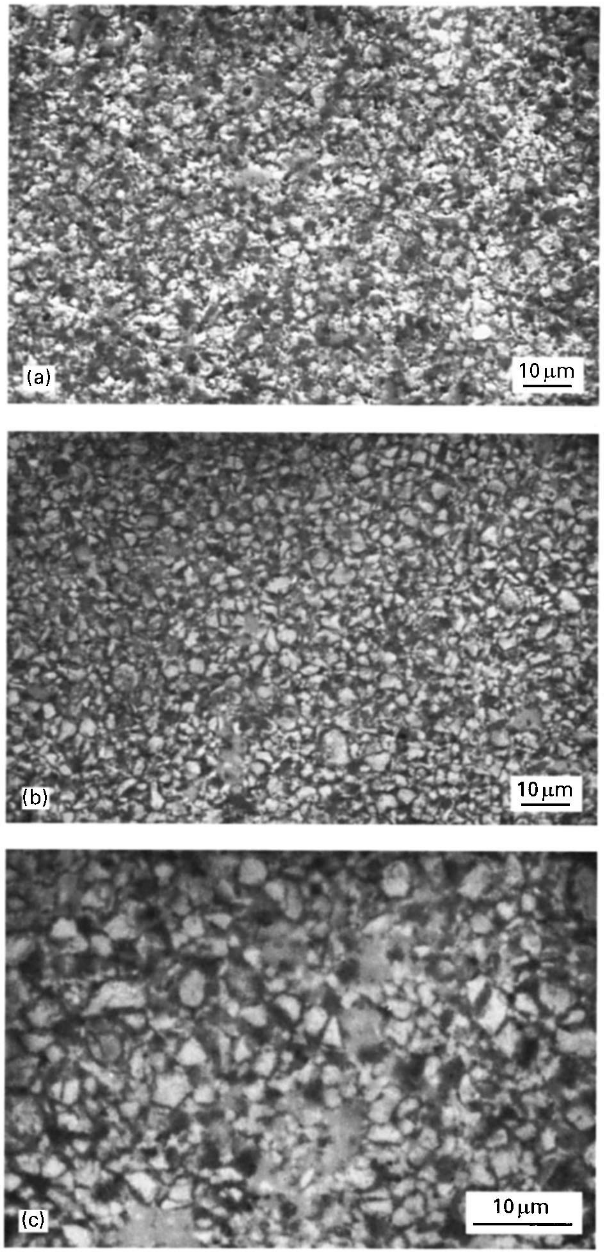

Figure 8 Alumina–TiN disc surface after a wear test of five runs of 72 000 cycles: (alumina, dark grey phases; TiN, white phases). (a) Microstructure in the unworn part, (b, c) Microstructure in the worn part (white–grey phases, mixed oxide phases).

In the case of alumina–TiN, the tribochemical contribution is very important. Indeed, there is clear evidence for the formation of titanium-based mixed oxide phases in the wear track. Such oxidation of TiN has already been observed during dry wear of alumina–TiN in contact with bearing steel under reciprocating sliding conditions [21] and wear of nitrogen-implanted alloys [22]. This tribochemical effect is consistent also with the smoothness of the wear track. Nevertheless, in the case of alumina, a smooth wear surface is often correlated with small grain size. The main results concerning the wear of alumina are that for an average grain size larger than 2 μm the dominant mechanism appears to be grain-boundary microfracture leading to grain chipping as noted above. For

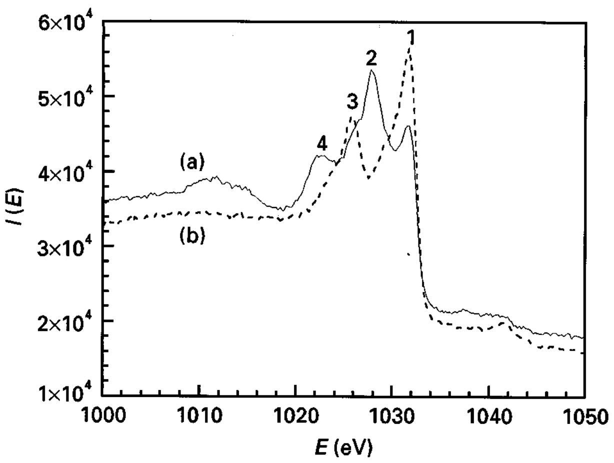

Figure 9 XPS spectra of the (a) worn and (b) unworn surface of the alumina–TiN composite 1–4, see text.

finer grain sizes, the worn surfaces are smooth and the tribochemical wear mechanism dominates [13, 19, 23]. Smooth surfaces would thus be indicative of a tribochemical wear process favoured by the small sizes of grains. In the case of alumina–TiN, grain size is small and should promote tribochemical reactions with an increase in the rate of oxidation. The observed chemical reactions might normally occur at very low rates but they are enhanced by the high-pressure, high-temperature conditions that exist at the interface between the friction partners [2, 3].

The absolute value of the friction coefficient during testing with alumina–TiN varies most probably in correlation with oxide formation as the friction coefficient is recognized to be independent of grain size [13]. Oxidation may be thought to produce a loosely adhering TiO_x or TiN_xO_y layer which is easily removed during sliding and the resulting rough surfaces lead to a higher level of friction. So the transition from low to high friction can be the result of competition between the kinetics of oxide layer formation and its removal by wear. The resulting rough surface is responsible for grooving of the alumina ball scribing on the composite. Another explanation may be the mixed oxide phases which form a very thin film and induce surface hardening [22, 24]. Frictional stresses causing deformation and microfracture in the solid and thin films and propagation of intra- and inter-granular fractures induce abrasive wear. This mechanism has also been observed during sliding wear of alumina–TiN composites [21]. All these observations show that the wear mechanism of alumina–TiN is a combination of tribochemical wear and abrasive wear.

Concerning the impact of the tribochemical effect, with alumina there is mechanical wear which is reduced by this tribochemical effect. With alumina–TiN composites, tribochemical interaction induces thin-film oxide formation which is regularly removed by abrasion from the wear system [18]. Although the wear mechanism is different for both systems, the results on wear volume are the same despite a higher friction coefficient for the composites, and during continuous tests the wear resistance of the composite seems greater. The wear resistance of alumina would be difficult to improve, but in the case of the composite the friction coefficient as well as the wear evolution depend strongly on the tribochemical wear, which is related to the TiN oxidation and to the removal of this phase. Therefore, it would, in principle, be easy to modify its wear resistance by adjusting the TiN content in the composite.

4. Conclusion

The alumina and alumina–TiN wear resistance in a corrosive medium which simulates living environments has been studied. The general wear mechanisms have been identified and two types of tribochemical interaction have been observed. Alumina is worn by mechanical wear with grain chipping. Water interacts at the wear interface, modifies the local contact stresses and decreases mechanical wear. With alumina–TiN, tribochemical reactions result in a reaction product which is alternately generated and removed from the wear interface by abrasion or peeling off. The wear volume values do not lead to a clear conclusion on the relative merits of both ceramics. The main difference between them is the friction coefficient of the composite, which is not regular and slightly higher. The wear mechanism of the composite shows that the presence of TiN is the major parameter and its wear behaviour should be easily modified by varying the TiN content.

Moreover, considering the increasing attention paid to tribochemical effects for surface finishing of engineering ceramics, the phenomena observed here could be used to produce composites with smooth surfaces. Such ceramics could then have very high potential as good tribological materials.

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