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The effect of residual stresses in functionally graded alumina–ZTA composites on their wear and friction behaviour

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Abstract

In this work we have evaluated the effect of compressive stress levels in functionally graded alumina–ZTA composites on their wear and friction behaviour during sliding in water. Neutron diffraction, X-ray diffraction and scanning electron microscopy were employed to analyze the samples and assess the acting tribological mechanisms. The results, which are compared to results from homogeneous alumina, show that with increasing residual compressive stresses in the samples of functionally graded material (FGM) both the wear and the friction are reduced. As a consequence of reduced crack formation and debris detachment from the surface (due to increased residual compressive stress) the tribochemical layer became thinner, with fewer topographical irregularities at the surface. This increases the role of the tribochemical actions compared to the mechanical wear, which beneficially affects the tribological performance in water.

Keywords: Wear resistance; Al_2O_3; ZrO_2; Biomedical applications; Functionally graded material

1. Introduction

Functionally graded materials (FGMs) provide a reasonable compromise in terms of the properties of materials that would not be possible to achieve otherwise. Good examples are ceramic hip-joints, normally made from alumina, a biocompatible and highly wear-resistant material, which, however, due to its limited strength presents an unacceptably high risk of fracture. As a result of this there have been various attempts to substitute alumina by zirconia in joint prostheses in order to overcome the main weak point of the alumina: its mechanical unreliability. However, these efforts produced rather disappointing results: the wear rate under such conditions was much higher than that observed for alumina.[1] Several studies of the wear of zirconia in an aqueous environment have suggested that Y-TZP materials may show strength degradation under certain conditions.[2,3] The material may undergo a phase transformation that affects its mechanical and wear properties. In other tests using a combination of alumina and zirconia in contact, the wear rate was lower, but the production of wear debris by microcracking still means that there are questions about the use of zirconia in such applications.[4]

Thus, varying the composition to provide a tough zirconia-rich core through to a hard, chemically and wear-resistant surface layer of alumina, offers a unique combination of properties, while retaining all the advantages of these materials.[5,6] The improved properties of such a functionally graded composite rely to a large extent on successfully shaping and sintering, and avoiding effects associated with the differential sintering of both materials. The higher shrinkage of zirconia when compared to alumina, as well as the mismatch of the coefficients of thermal expansion, may result in residual stresses within the composite. This gives a certain risk of crack formation; while on the other hand, a beneficial effect on the wear behaviour due to the compressive stresses in the alumina surface layer can be expected. Hence, a good stress balance within the graded composites is required to beneficially affect the overall behaviour of the part.

The objective of this work was to evaluate the residual stresses in step-graded Al_2O_3–ZTA composites for functionally graded artificial hip-joints prepared by sequential slip-casting, and to

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establish their effect on the wear and friction behaviour. The results are compared with results for homogeneous alumina ceramics.

2. Experimental

Step-graded discs (samples AZ-1 to AZ-3), which were 36 mm in diameter and 5-mm thick, and ball-head samples with a diameter of 32 mm were prepared by sequential slip-casting of aqueous suspensions with various compositions, as presented in Table 1. The starting aqueous suspensions of the various compositions were prepared from alumina (Alcoa A16 SG, mean particle size 0.7 μm) and zirconia powders (Tosoh, TZ-3Y, mean particle size 0.3 μm) by homogenisation in an attrition mill with the addition of a deflocculant, Dolapix CE64 (Zschimmer & Schwarz, Leinstein). The green parts, composed of three or seven layers with increasing zirconia content towards the core (see Table 1), were sintered at 1550 °C for two hours, HIP-ed for 20 min at 1390 °C in 140 MPa Ar and mechanically polished. For a comparison homogeneous alumina discs of the same size (Sample A) were also used in this investigation.

The stress level in the Al_2O_3 at the surface was measured by X-ray diffraction analysis (XRD, Siemens D500, Germany), performed with Cu Kα radiation (40 kV, 40 mA). The {1 4 6} reflection of $\alpha-Al_2O_3$ was investigated. The tilt angle of the sample with respect to the X-ray beam, Ψ^2, was varied from 0 to 0.8 in steps of 0.1. The 2θ angle of diffraction was varied between 134 and 138° in steps of 0.02. For the elastic constants Poisson's ratio $\nu_{\{1 4 6\}}$ and Young's modulus $E_{\{1 4 6\}}$, 0.27 and 356 GPa were used, respectively.

The stress profile through the thickness of the discs was evaluated by neutron diffraction. The method for the latter is based on an experimental examination of the two components of the lattice strain tensor. The experimental arrangement used for strain scanning of the axial ε_z and radial ε_x components of the strain tensor in the step-graded disc is fully described in reference.[7]

The wear tests were performed in a TE77 device (Phoenix Tribology Ltd, Newbury, England) that produced reciprocating sliding with a 7-mm stroke length at a frequency of oscillation of 1 Hz and a load of 50 N. The test duration was 2 h, resulting in a total sliding distance of about 100 m. Before each test polished specimens ($R_a = 0.05 \pm 0.01$) were carefully cleaned in an ultrasonic bath with ethanol and then dried in a stream of air. The discs were fixed in an epoxy-resin holder and immersed in distilled water. The counter bodies, i.e., the upper specimens in these tests, were standard 10-mm balls of homogeneous alumina. They were mounted in a reciprocating holder and pressed against the testing disc (step-graded samples or homogeneous alumina) with the selected load via a stationary loading system. The coefficient of friction was continuously monitored during the test. After the test, the samples were dried in a stream of air. Wear scars on the discs were first examined by means of an optical microscope (Ernst Leitz Wetzlar GmbH, Wetzlar, Germany) and a stylus-tip profilometer (T8000, Hommel Werke GmbH, Schwinningen, Germany). The wear volume of the wear scars was calculated by multiplying the average (five measurements in every wear scar) cross-sectional area of the scar with the stroke length. All the experiments were repeated at least three times. The measurements were statistically evaluated and the average values and standard deviations were calculated. Selected samples were sputter coated with gold and examined under the SEM (Jeol T330A, Tokyo, Japan).

Table 1
Compositions of the disc samples

Sample	Number of layers	Composition of the layers (vol.%)
A	1	Al_2O_3
AZ-1	3	Al_2O_3 70% Al_2O_3/30% ZrO_2 Al_2O_3
AZ-2	7	Al_2O_3 86% Al_2O_3/14% ZrO_2 78% Al_2O_3/22% ZrO_2 70% Al_2O_3/30% ZrO_2 78% Al_2O_3/22% ZrO_2 86% Al_2O_3/14% ZrO_2 Al_2O_3
AZ-3	3	Al_2O_3 78% Al_2O_3/22% ZrO_2 Al_2O_3

3. Results and discussion

The differences in the total sintering shrinkage and in the coefficients of thermal expansion for the alumina and ZTA result in dimensional changes during the heating and cooling cycles of the sintering. Recently, we reported[8] that the total sintering shrinkage of the different layers in step-graded composites can be partly compensated by a modification of the particles' surface charge by adjusting the pH of well-dispersed starting suspensions. In contrast, the dimensional change during cooling from the sintering temperature cannot be effectively controlled. The result is a stress gradient with residual tensile stresses in the zirconia-containing core and compressive stresses in the outer alumina layer.[9] The stress profiles determined for the sintered and HIP-ed samples prepared in the present investigation, i.e., for the step-graded discs with three (sample AZ-1) or seven layers (sample AZ-2), are presented in Fig. 1a and b, respectively. The graphs show that residual tensile stresses up to 150 MPa remained in the core of both samples, while in the alumina surface layers compressive stresses up to −100 MPa were detected. Comparing the results in both figures, one can see that the stress gradient is slightly higher for the sample with three layers (AZ-1), even though the zirconia content in the core material was the same for both samples. In the 7-layered sample (AZ-2) the compressive and tensile stresses at the interfaces of the layers of dissimilar materials are obviously partly compensated, resulting in an apparently continuous stress gradient. No cracks were observed in the sample with 7 layers (Fig. 1d), while a thin crack in the core of the 3-layered sample AZ-1 was detected (Fig. 1c), which suggests that the tensile stress exceeded the critical value.

In order to evaluate the effect of the observed compressive stresses at the polished alumina surface on the wear behaviour

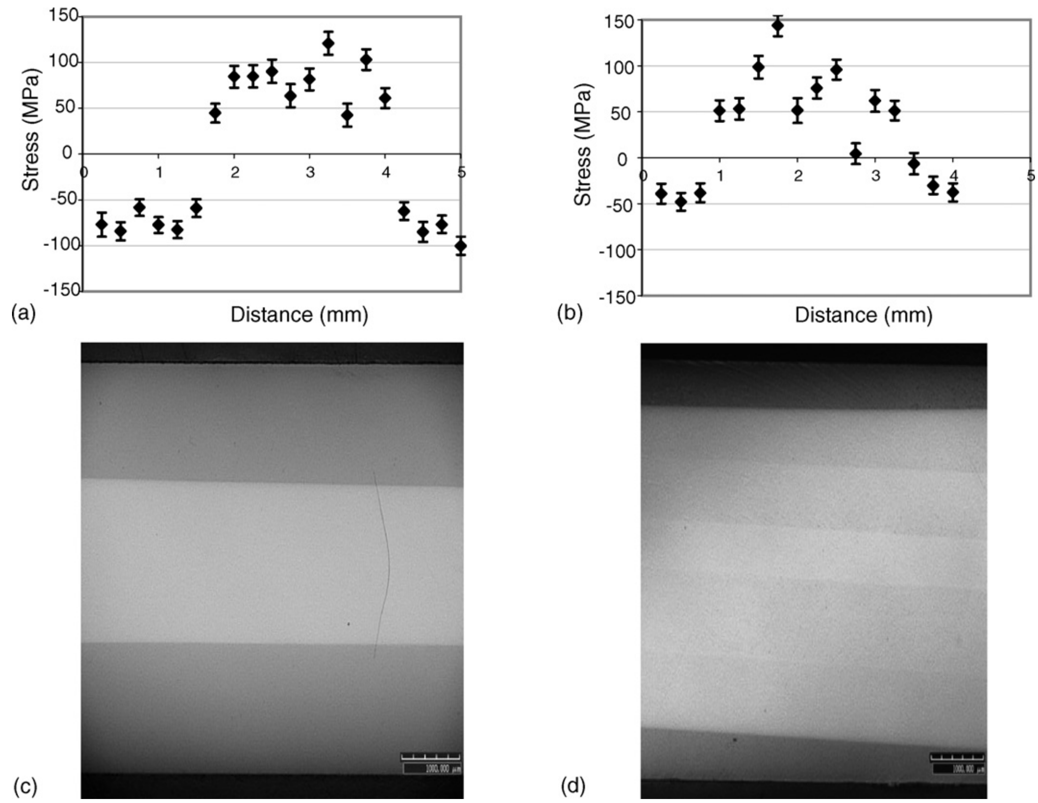

Fig. 1. The stress profile for the step-graded discs with three (a) or seven layers (b); (c) and (d) optical micrographs of their polished cross-sections, respectively.

of the composites, samples with different stress levels were analyzed and compared to homogeneous alumina. The stress level at the alumina surface for the discs with different compositions was measured by X-ray diffraction at different points across the sample surface and the results are presented in Table 2. In contrast to pure alumina, where no residual stress is present, high compressive stresses were detected at the surface of the polished step-graded discs. The measured stress values were somewhat higher than observed with neutron diffraction analysis of the samples before machining (see Fig. 1).

The compressive stress in the alumina surface layer of the samples AZ-2 (7-layered sample with 30 vol.% ZrO_2 in the core) was only slightly lower than that for the 3-layered AZ-1 with the same ZrO_2 content in the core, while the stress was much lower for the 3-layered sample AZ-3 with a lower ZrO_2 content, i.e., 22 vol.%. This confirms that the zirconia content has a major effect on the stress level in the functionally graded composites.

The tribological behaviour of the homogeneous alumina and the step-graded alumina–ZTA discs is presented in Fig. 2a and b as the coefficient of friction and the wear volume after 2 h of sliding in water. It is obvious that the residual stresses affect both the friction and, in particular, the wear behaviour of the discs with alumina at the surface. As expected, higher compressive stress results in a lower wear volume. In a first approximation this was ascribed to the hindering effect of the compressive stress on the formation and propagation of any cracks created as a result of the mechanical action during sliding. The SEM investigations of the wear tracks revealed that in all the samples, i.e., in the homogeneous alumina as well as in the step-graded samples, the worn surface was covered with rather smooth tribolayers, without any evidence of distinctive mechanical wear, see Fig. 3.

Such an observation is in agreement with the typical appearance of the layers that cover worn surfaces under predominantly tribochemical wear mechanisms.[10–12] On the other hand, residual stresses affect primarily the crack formation and the subsequent mechanical wear mechanisms. From Fig. 3a and c, showing the wear scars of the homogeneous alumina sample (A) and of the step-graded sample with highest residual stress in the alumina surface layer (AZ-1), one can see that the number of cracks in the tribolayer of homogeneous alumina (Fig. 3a) is larger than for the step-graded sample (Fig. 3c). The corresponding enlarged areas presented in Fig. 3b and d support this observation. Since these cracks are most probably formed during drying after the tests,[13] this suggests that the layers become thinner as the residual stress increases. The tribolayers that form on ceramic surfaces in aqueous solutions are mainly composed of detached small-scale wear debris that are tribochemically transformed and embedded in hydroxide and/or other amorphous

Table 2
Compressive stresses at the surface of the discs with different composition

Sample no.	No. of layers	ZrO_2 content in the core (vol.%)	Compressive stress at the alumina surface (MPa)
A	1	0	0
AZ-1	3	30	-260 ± 5
AZ-2	7	30	-241 ± 5
AZ-3	3	22	-175 ± 4

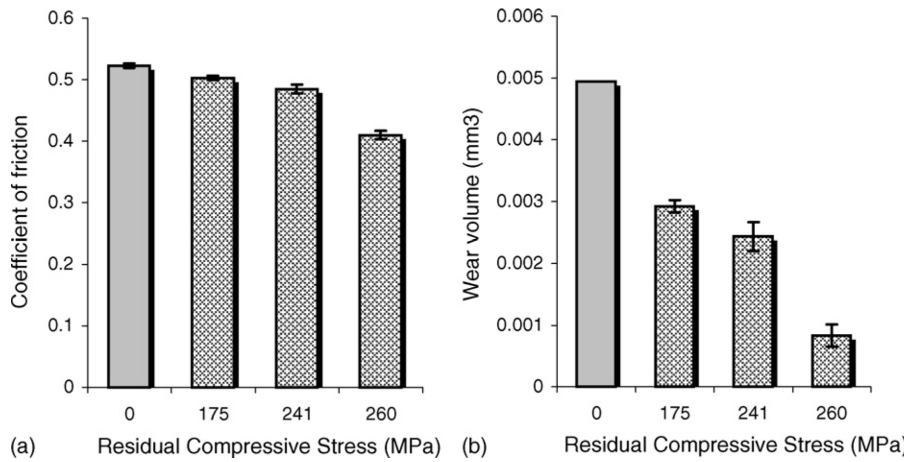

Fig. 2. The wear volume (a) and coefficient of friction (b) for the discs with different residual compressive stresses at the surface in distilled water.

phases to form a tribolayer.[11–14] Therefore, it seems reasonable to conclude that the higher compressive residual stresses that inhibited crack formation in the ceramic samples also produced a smaller amount of wear debris that can be released from the surface and subsequently be embedded and form the top surface tribolayer. The evidence of the amount of cracks, the visual appearance of the layers (Fig. 3) and the amount of wear volume (Fig. 2), which are consistently lower as the residual stresses in the samples increase, all support this explanation. In addition, the coefficient of friction also decreases with increased residual stresses (see Fig. 2a), as a result of the reduced amount of wear debris and their size, and consequently the increased role of the tribochemical layer in comparison to mechanical wear. Therefore, as the stresses increase, the observed tribochemical layers are smoother and with less irregularities, which also leads to a lower coefficient of friction.[14]

The formation of the tribolayer during the sliding wear of alumina ceramics in wet environments has been reported elsewhere.[11,12] It was established that the tribolayer formation, its composition and thickness depend significantly on the pH of the liquid in which the wear test is performed.[14,15] Thick tribolayers and high wear rates are, in particular, characteristic for slightly alkaline and near-neutral pH conditions, like those used in this work (distilled water). At slightly lower pH values, i.e., approximately 4–6, the wear rate was reported to be lower, and thinner tribolayers were formed. Hence, for a better prediction of the tribological behaviour of the step-graded composites used in biomedical implants, further analysis in biological-like environments is still needed.

It is worth mentioning that in comparison with zirconia the observed wear rate for the step-graded composites with an alumina surface layer was an order of magnitude lower under

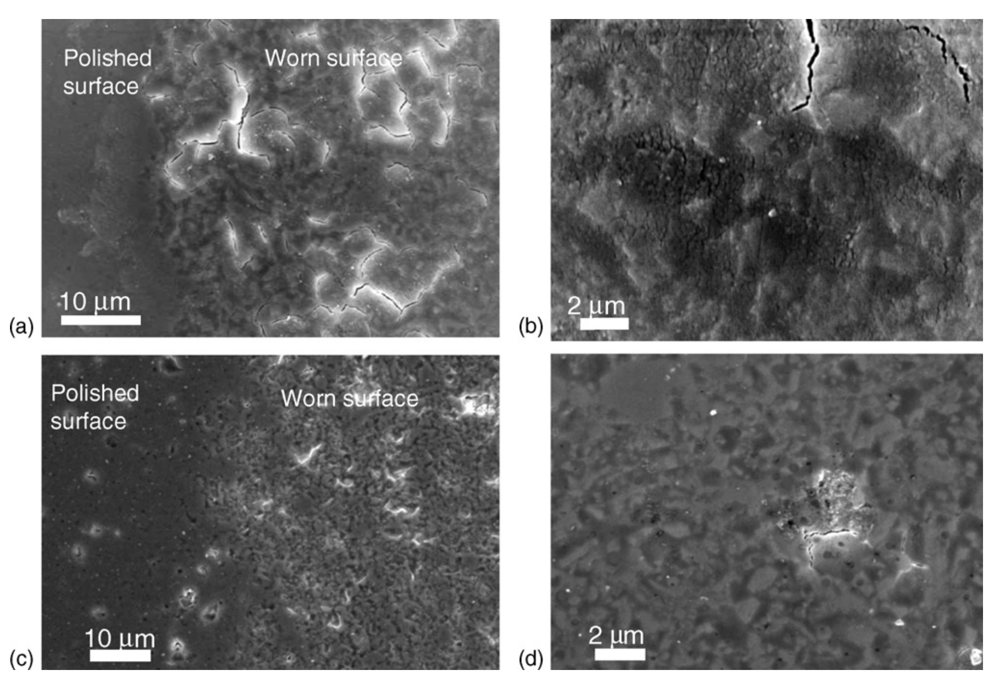

Fig. 3. SEM micrograph of the wear tracks in the homogeneous alumina (a, b) and on the step-graded A-ZTA-A discs (c, d).

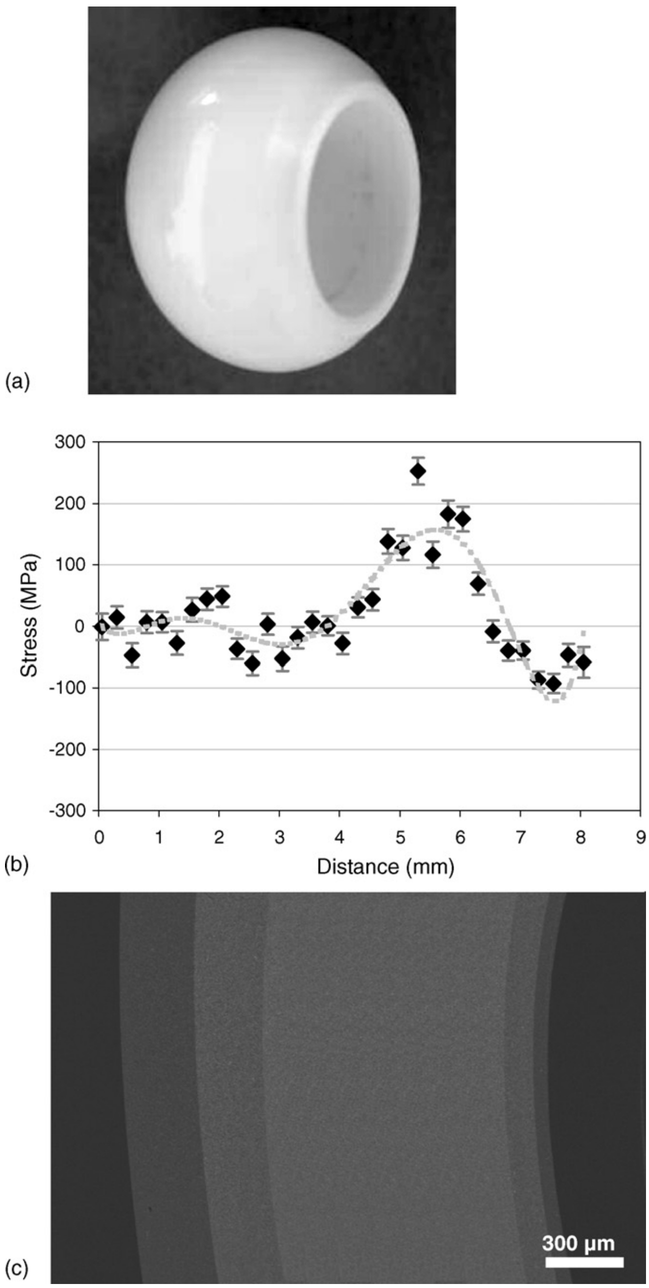

Fig. 4. (a) Ball-head of the hip-joint, near-net shaped by sequential slip-casting (surface finishing by Ceramtec, Plochingen, Germany); (b) the stress profile and (c) SEM micrograph of the cross-section.

the same conditions.[16,17] This is primarily caused by the tribochemically promoted phase transformation of zirconia. The transformation induces deterioration in the mechanical properties, and the resulting lower wear resistance puts into question the application of zirconia as a material for body implants that are subjected to wear.

Fig. 4a–c present a slip-cast, sintered, HIP-ed and machined sample of the ball-head for a hip-prosthesis with a functionally graded composition, the stress profile and SEM micrograph of its cross-section, respectively. As presented, the stress profile is similar to the discs with 7-layers, which would lead us to expect similar wear behaviour. The X-ray analysis at the surface of the ball-head after machining confirmed a residual compressive stress of -130 ± 10 MPa. A systematic examination of the samples' cross-sections revealed, however, that due to a high zirconia content in the core and the resulting high compressive stresses, the occasional formation of cracks in the tensile stressed core may be a critical drawback of such compositions. This accords with the suggestion of Gasik,[9] that the safe limit for the compressive stress is below 150 MPa for symmetrically graded ball-heads. Further, he stressed that a proper compositional profile is of decisive importance to avoid crack formation in FGMs. Hence, in order to ensure the optimal behaviour of the functionally graded composites, there should either be a strict control of the compositional profile or, better, the zirconia content in the core should be limited to approximately 22 vol.%.

4. Conclusions

Step-graded ceramic composite samples composed of a ZTA core and an alumina surface with three to seven layers were prepared by the sequential slip-casting of aqueous suspensions with compositions that enable minimal mismatch in the sintering shrinkage between the layers. The neutron diffraction analysis revealed that the residual tensile stresses in the zirconia-containing core are higher than the compressive stresses in the alumina surface layer. Accordingly, X-ray analysis confirmed the residual compressive stress at the surface of the step-graded samples to be in the range of 175–241 MPa for the samples with 22–30 vol.% of zirconia in the ZTA core material.Both the wear and the friction decreased with an increase in the compressive-stress level. The observed beneficial tribological behaviour is due to crack nucleation and propagation reduction as a result of compressive stresses at the outermost alumina layers, which are generated in combination with a tensile-stressed ZTA core. This results in thinner and smoother tribochemical layers, which beneficially affect the tribological performance of ceramics in an aqueous environment, as already reported by others and ourselves.The beneficial effect of the compressive stresses at the surface on the wear behaviour of FGMs in bio-implants (artificial joints) should, however, be critically evaluated with regard to the probability of the tensile stress exceeding the critical value for crack formation. The results of this work suggest that the zirconia content in the core should be below 22 vol.% to limit the residual stresses leading to crack formation. Hence, an optimal stress balance is needed to obtain the overall beneficial effect of the functionally graded composites.

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