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Effects of Grain Size and Ceria Addition on Ageing Behaviour and Tribological Properties of Y-TZP Ceramics

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Abstract

The influence was investigated of ceria addition and the grain size on ageing and wear behaviour of Y-TZP ceramics. Two types of ceramics were studied: ZY5 (95 mole% ZrO_2 and 5 mole% $YO_{1\cdot5}$) and ZY4Ce4 (92 mole% ZrO_2, 4 mole% $YO_{1\cdot5}$, and 4 mole% CeO_2). Each ceramic was sintered with grain sizes of 0·18 μm (95% dense) or 0·5 μm (98% dense). Only the ZY5 ceramic with a grain size of 0·5 μm showed degradation to monoclinic zirconia (= ageing) after a treatment in water at 180°C. This ceramic was also the only one in which a phase transformation was observed after wear tests in water for a pin (SiC) on plate test configuration. However, this transformation was found not to affect the wear rate. Wear mechanisms were investigated for testing in dry nitrogen and water environment.

1 Introduction

Modern technical ceramics such as ZrO_2, Al_2O_3, Si_3N_4, and SiC are suitable for application as wear resistant parts.[1–3] Generally, these materials have a high hardness and Young's modulus, they are chemically inert, and can be used at high temperatures if compared with metals. However, in case of severe local contact the brittleness of ceramics can lead to rapid wear by surface microfracture.[4] According to Fischer *et al.*, a relation exists between wear behaviour and toughness of brittle materials.[5]

Yttria-stabilised tetragonal zirconia polycrystalline (Y-TZP) ceramics have excellent strength and good fracture toughness. However, these materials show a spontaneous phase transformation to monoclinic zirconia, which is dependent on grain size.[6–10] Under influence of water at elevated temperatures ($\geq$ 200°C) this phase transformation can take place very fast.[11] On the other hand, Ce-TZP ceramics have an improved stability of the tetragonal phase and show a good fracture toughness, but its strength is lower and the dynamic grain growth is very strong.[6,7,12,13] For these reasons TZP ceramics with a good resistance against ageing, good formability, and excellent mechanical properties can be fabricated using yttria and ceria as stabiliser for the tetragonal phase.

Ageing of TZP ceramics can have a strong influence on the wear resistance in water at temperatures of 150–250°C.[14] Even at room temperature frictional heating may, depending on the tribological conditions, lead to locally confined high temperatures: so-called flash-temperatures.[15]

The present paper describes the influence of ceria on the tribological behaviour of two types of Y-TZP ceramics when tested under dry and aqueous conditions. One material (ZY5) shows a degradation on ageing while the other (ZY4Ce4) has an improved resistance to ageing in water. In

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addition, the influence was examined of grain size on the tribological and ageing behaviour.

2 Experimental Procedure

Powders of the tetragonal zirconia ceramics ZY5 (ZrO_2 with 5 mole % $YO_{1.5}$) and ZY4Ce4 (ZrO_2 with 4 mole % $YO_{1.5}$ and 4 mole % CeO_2) were prepared by a gel precipitation technique using metal chlorides as precursor chemicals. This preparation process is described in detail by Groot Zevert *et al.*[16] The green compacts of both powders were pre-pressed isostatically at 50 MPa, then ground in a mortar, and subsequently uniaxially pressed at 80 MPa in a 40×8 mm mould. Finally, the compacts were isostatically pressed at 400 MPa and sintered in a tube furnace at 1150°C for 10 h (heating and cooling rate 2°C min^{-1}). The relative density after this sintering procedure is 95–96% for both ZY4Ce4 as well as ZY5 compacts. An average grain size of 0·18–0·19 μm for both ceramics was determined using the linear intercept technique[17] on SEM photographs. A relatively large grain size of 0·5 μm was obtained for ZY4Ce4 and ZY5 compacts after sintering at 1400 and 1450°C for 2 h, respectively. The relative density after sintering at these temperatures is 98% for both specimens.

The sintered compacts were sawn in bars of 2×2×5 mm (ageing experiments) or of 25×5×2 mm (tribological experiments). The bars, used for tribological measurements, were polished on one side with 0·05 μm alumina powder, followed by ultrasonic cleaning in ethanol for about 45 min. To remove stresses introduced by machining and polishing all the bars were annealed at 950°C for 10 min (heating and cooling rate 2°C min^{-1}).

Ageing experiments were performed in an autoclave with the samples put in a PTFE vessel filled with double-distilled water. An initial nitrogen pressure of 30 bar was applied and the samples were kept at a temperature of 180°C for 5 h. The fraction of the monoclinic phase compacts was determined, before and after hydrothermal ageing, by X-ray diffraction (XRD), using a diffractometer PW 1710 with CuK_α radiation. The integrated intensities of the diffraction peaks were obtained by stepwise counting the intensity using a step-size of 0.025°(2θ) and a counting time of 5 s. Intensities were corrected for background. The monoclinic volumetric fraction V_m was calculated using Toraya's equation.[18]

In the wear study, tribological systems were investigated of a polished SiC sphere (diameter: 4 mm) sliding sinusoidally against TZP plates. The track length was 10 mm, the sliding frequency 4 Hz (the maximum velocity is 0·125 m s^{-1}), and the normal load 8 N (an initial Hertzian pressure of 815 MPa) for a testing time of 16–20 h corresponding to a sliding distance of 4·6–5·8 km. Testing occurred at room temperature in either distilled water or in dry nitrogen (<1 % relative humidity) atmosphere.

The total vertical displacement of the SiC ball during sliding was measured by a extensometer (Sangamo DG1; sensitivity 1% or 1 μm) and the friction force by a force transducer. The displacement and friction force were simultaneously sampled under external triggering control with a computerised data acquisition system. The vertical displacements were averaged and the force signal was processed using autocorrelation and fast fourier transformations. The friction coefficient was estimated according to:[19]

$$f = \frac{(Q_1 + Q_3 + Q_5)^{1/2}}{F} \tag{1}$$

with Q_i the ith harmonic of the autopower spectrum of the force signal and F the normal load. Higher order harmonics were neglected.

The wear rate K_w was evaluated using the following equation:

$$K_w = \frac{W_m}{\rho \cdot L \cdot F} \tag{2}$$

with W_m is the mass loss during wear testing (absolute accuracy $5{\cdot}10^{-5}$ g), ρ is the density of the material, L the length of the wear path, and F the normal load. Alternatively, the volume loss was determined by measuring the wear profile. To obtain a good approximation of the volume loss, the profile depth and width were measured using a profilometer (Slorn, Dek-Tak 3030, Santa Barbara, USA) with the profile measured in the sliding direction of the wear track and on three places perpendicular to the sliding direction (middle, and both edges of the wear track).

The worn surface and wear debris were analysed by X-ray diffraction (XRD), using a diffractometer PW 1710 with CuK_α radiation, and energy dispersive analysis of X-ray (EDX) techniques using a Kevex Delta class III mounted on a Jeol scanning electron microscope (SEM), type JSM 35CF. The surface roughness of samples before and after wear testing were measured with a profilometer (Slorn, Dek-Tak 3030, Santa Barbara, USA). The worn scales were examined using SEM pictures.

3 Results and Discussion

3.1 Ageing behaviour

Before the ageing experiments the crystal structure of both ZY4Ce4 and ZY5 with small (0·18 μm) and large (0·5 μm) grain sizes (codes S and L, respectively) is fully tetragonal as determined by X-ray diffraction. The monoclinic volumetric fraction after the hydrothermal ageing test is show in Table 1. These results indicate that the ageing resistance of Y-TZP strongly depends on both grain size and composition. A fine grained microstructure and the use of ceria as extra dopant improves the resistance against ageing, which is in agreement with the results of Boutz.[6]

3.2 Friction coefficient

For the wear tests it is necessary that the conditions are such that the water lubricated tribosystem is in the boundary lubricated regime (Schipper *et al.*[20]) because otherwise not only the wear behaviour is investigated but also other phenomena are present in the data. To check this the so-called lubrication number,[20] L, a dimensionless quantity, is used:

$$L = \frac{\eta \cdot V_+}{p \cdot R_t} \tag{3}$$

where η is the viscosity of the lubricant (water at 20°C: $1{\cdot}10^{-3}$(Pa.s)], V_+ the relative velocity of the two surfaces [(0·125 (m s^{-1})], p the effective mean contact pressure, and R_t is the combined surface roughness of the two contact surfaces. The latter quantity is defined by:

$$R_t = \sqrt{R_1^2 + R_2^2} \tag{4}$$

where R_1 and R_2 are the centre line average roughness values of surfaces 1 and 2, respectively. To check the test conditions we calculated the lubrication number for one of our experiments. The initial Hertzian pressure, p, is 815 MPa, the initial combined surface roughness, R_t, is 100 nm for the ZY5/L sample. Thus the initial lubrication number is $1{\cdot}53 \times 10^{-6}$. The lubrication number at the end of this experiment was found to be $6{\cdot}8 \times 10^{-5}$, resulting from a final effective mean pressure of 13·7 MPa (calculated from a final contact plane radius of the SiC ball of 0·43 mm and a force of 8N) and a roughness, R_t, of 147 nm. This means that the whole experiment is performed in the boundary lubricated regime.[20]

The friction coefficients of the various experiments are shown in Table 2 and it is seen that:

- the friction coefficient is lowered for the samples tested in water which is expected for a lubricated system. So during these experiments a lower shear stress is applied on the TZP plates;
- the friction coefficient is lower for the ZY4Ce4 than for ZY5 sample for the samples tested in N_2, but this result cannot be explained;
- a small decrease in friction coefficients is measured for plates with an increasing grain size, independent on the chemical composition, for the samples tested in N_2.

Table 1. Monoclinic zirconia content (V_m) after ageing at 185°C for 5 h in water

Sample code	*Grain size (μm)*	*V_m (%)*
ZY4Ce4/S	0·19	0
ZY4Ce4/L	0·50	0
ZY5/S	0·18	0
ZY5/L	0·50	89

3.3 Wear behaviour in dry condition

The specific wear rates of the TZP plates and SiC balls after testing in dry N_2 are depicted in Table 3. No monoclinic zirconia phase is detected on the TZP plates before and after completion of the test. From these results it is concluded that, if one regards the lower porosity, larger grain sizes result in a larger specific wear rates for both ZY4Ce4 and ZY5 ceramics This increase in wear rate with increasing grain size is in agreement with the results of He *et al.*,[21] where a Hall–Petch type of relationship ($d^{-1/2}$) is observed between wear resistance and grain size.

The specific wear rate of the SiC balls is smaller when sliding against ZY5 samples as compared to ZY4Ce4 as counter material (Table 3). The wear

Table 2. Friction coefficients after sinusoidal sliding in N_2 or water environment

Material	*N_2:f (begin–end)*	*Water f (begin–end)*
ZY4Ce4/S	0·46–0.40	0.27–0.13
ZY4Ce4/L	0·37–0·38	0·30–0·15
ZY5/S	0·56–0·51	0·29–0·24
ZY5/L	0·50–0·47	0·21–0·16

Table 3. Specific wear rates of the TZP plates and SiC for sinusoidal sliding in N_2 environment

Material	*K_w (10^{-6} mm^3 N^{-1} m^{-1}) profilometer*	*K_w (10^{-6} mm^3 N^{-1} m^{-1}) weighing*	*K_w (10^{-6} mm^3 N^{-1} m^{-1}) SiC ball*
ZSY4Ce4/S	1·6	2·3	4·5
ZY4Ce4/L	2·8	2·5	3·4
ZSY5/S	1·0	0·9	2·4
ZY5/L	1·2	1·7	2·8

rate of the ZY5 plates is also smaller as compared to the ZY4Ce4 plates suggesting that the specific wear rate of the SiC balls is related to the specific wear rate of the TZP plates. This relation is also published by He *et al.* for TZP ceramics[21] and for ADZ (20 wt% Al_2O_3 dispersed in Y-TZP).[22]

The wear mechanisms as determined by the morphologies are the same for all materials and are independent of chemical composition and grain size. Using the temperature maps as given by Ashby[15] both bulk and flash temperatures during the tribological test can be obtained. Because of the low sliding speed (maximum of $0{\cdot}125\,m\,s^{-1}$) the maximum value of the surface and flash temperature is about 100°C of the TZP/SiC couple. It is therefore not expected that thermal cracking occurs during the tribological tests. The surface morphologies indicate that plastic deformation, microcracking (caused by fatigue), microcutting or microploughing (predominant in the middle of the wear track), and adhesion of wear debris occur during these sliding tests in nitrogen environment. Plastic deformation is more pronounced at smaller grain sizes.[21] Microcracks (caused by fatigue) perpendicular to the sliding motion (Fig. 1) are observed all over the wear track but its concentration is significantly larger at the turning points. The increase of microcracks at the turning points can be explained by the fact that the static friction coefficient is larger than the dynamic friction coefficient. This means that the tangential force (and therefore the shear stress) has its largest value at the turning points. Wear debris adheres to the TZP plates followed by plastic deformation of the adhered surface layer, as depicted in Fig. 2.

3.4 Influence of water on wear behaviour

Under water environment the specific wear rates of ZY5 and ZY4Ce4 ceramics are very low. The wear rates of the samples with a large grain size (and a larger density) are slightly larger as compared to the samples with a small grain size. According to Table 1, ageing occurs for ZY5/L (grain size $0{\cdot}5\,\mu m$). The ageing also has been determined after the wear test on the ZY5/L sample in water (Table 4).

Like in the dry N_2 wear tests, the friction coefficient decreases with increasing grain size for both types of TZP ceramics when tested in water (Table 2). The opposite trend, however, was observed by Zum Gahr *et al.*[23] whose tests on zirconia were performed on other tribological systems (block on ring and ring on block). This indicates an influence of the tribosystem on the relation between friction coefficient and grain size.

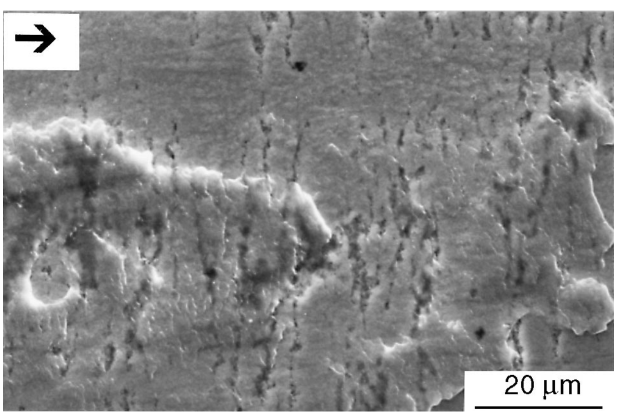

Fig. 1. Morphology of ZY5/S after sliding in N_2. Microcracks, caused by fatigue, are observed perpendicular to the sliding direction. Arrow indicates one direction of the reciprocal sliding.

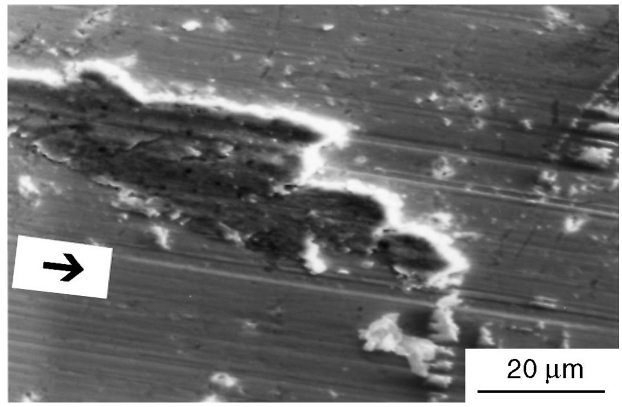

Fig. 2. Morphology of ZY4Ce4/S after sliding in N_2, showing abrasive wear (microcutting/microploughing) and plastic deformed wear debris. Arrow indicates one direction of the reciprocal sliding.

Table 4. Specific wear rates of TZP and SiC and monoclinic fraction zirconia on the plate surface after sliding wear in water

Material	K_w $(10^{-6}\ mm^3\ Nm^{-1})$ *TZP*	K_w $(10^{-6}\ mm^3\ Nm^{-1})$ *SiC ball*	V_m (%)[a]
ZY4Ce4/S	≪0·01	≪0·01	0
ZY4Ce4/L	0·03	0·70	0
ZSY5/S	≪0·01	≪0·01	0
ZY5/L	0·03	0·60	15–20

[a]Initial fraction monoclinic zirconia is 0% for all samples.

Table 5. The centre line average roughness of the TZP ceramics after wear tests. The measurements are taken in the length of the wear track and in the width of the wear track in the middle of the plate

Material	*Water*		*Dry N_2*	
	R_A (nm) length of wear track	R_A (nm) width of wear track	R_a (nm) length of wear track	R_a (nm) width of wear track
ZY4Ce4/S	310	121	1454	3165
ZY4Ce4/L	167	105	1617	4219
ZY5/S	476	196	1796	2765
SY5/L	115	111	2126	2636

The roughness of the TZP plates after the wear test in water is less if compared with values after tests in a dry N_2 environment (Table 5). This difference can be explained by a difference in wear mechanisms. In none of the water tested samples fatigue is found as a wear mechanism indicating that the lubrication of water is sufficient to reduce significantly the shear strain on the TZP ceramics. This also is corroborated by the reduced coefficient (Table 2).

On ZY4Ce4/S the main wear mechanism is based on abrasion (microcutting, microploughing) but its presence is strongly reduced as compared to the same sample tested in a dry environment. Grain pull out is a minor mechanism on this material.

For the ZY5/S specimen the predominant mechanism is grain pull out while the minor mechanism is abrasion (Fig. 3). Also some small random orientated cracks are observed on the surface of this material indicating that these cracks are not caused by shear stress. The wear debris sticks on the surface of this sample.

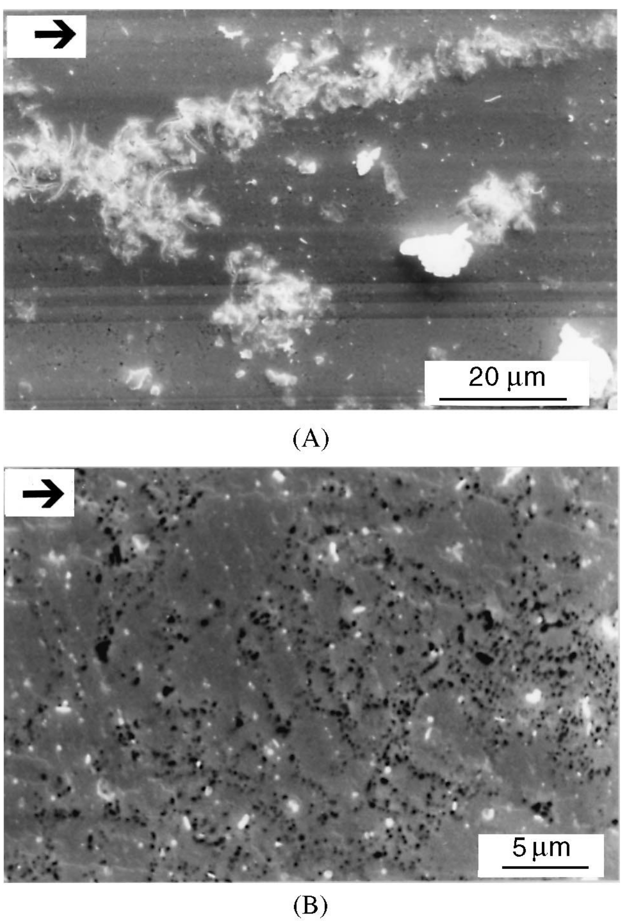

Fig. 3. Scanning electron micrographs of ZY5/S plate (grain size of 0.18 μm) after sliding test in distilled water. (A): very smooth surface is observed after sliding. Soft abrasive wear is shown all over the sample, together with some small random orientated cracks. The white particles are some dirt particles sticked on the sample. (B): high magnification shows that the black holes are caused by grain pull out. Arrow indicates indicates one direction of the reciprocal sliding.

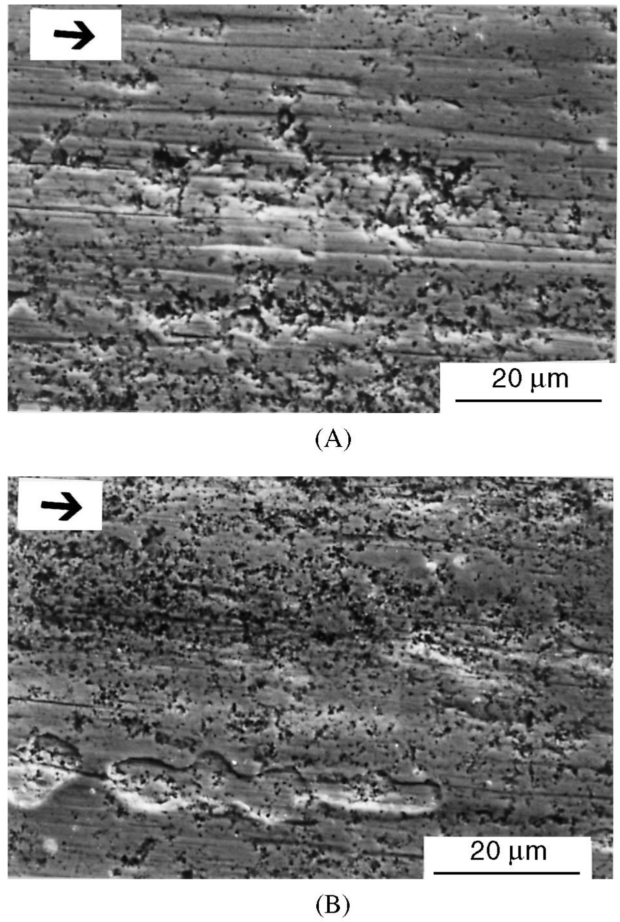

Fig. 4. Scanning electron micrographs of ZY5/L with grain size of 0·50 μm after sliding test in distilled water. (A): abrasive wear (B): delamination of the thin layer is shown on the contact surface. Grain pull out becomes a main wear mechanism by the intergranular microfracture. Arrow indicates indicates one direction of the reciprocal sliding.

Grain pull out is also the main mechanism for the samples with a larger (0·50 μm) grain size: ZY5/L (Fig. 4) and ZY4Ce4/L (Fig. 5). This mechanism is even more pronounced than in the ZY5/S sample. Grain pull out mechanism seems to increase with increasing grain sizes. The removed grains act as a third body resulting in an increase of abrasive wear in the centre of both the ZY5/L and the ZY4Ce4/L material. As a result this third body wear causes an increase of the wear rate when compared with the samples with a small grain size (Table 4). Furthermore, delamination takes place on the contact surface of ZY5/L and ZY4Ce4/L. On the ZY5/*L* specimen the same random orientated cracks as on the ZY5/S sample are present but they occur in larger quantities.

Tetragonal zirconia transformation occurred in the ZY5/L sample, during testing in water. This transformation was already expected from the ageing results (Table 1) but does not influence the wear behaviour if compared to the ZY4Ce4/L material, which does not show any phase transformation and has the same wear rate. This ageing

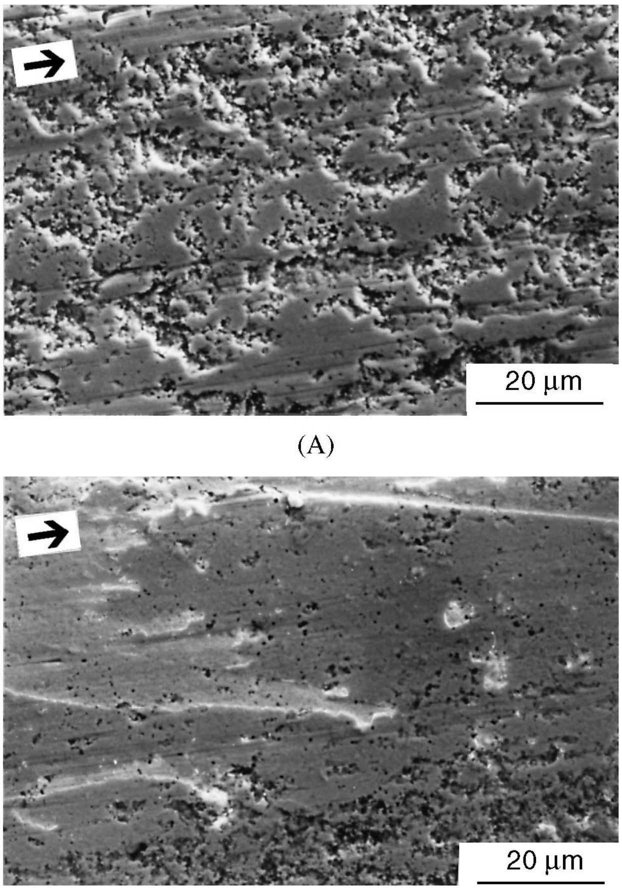

Fig. 5. Scanning electron micrographs of ZY4Ce4/L with grain size of 0·50 μm after sliding test in distilled water. (A): abrasive wear and microfracture. Grain pull out becomes a main wear mechanism by the intergranular microfracture. (B): delamination of the thin layer is shown on the contact surface. Arrow indicates indicates one direction of the reciprocal sliding.

transformation during sliding can be an onset for higher wear rates, especially at more extreme tribological conditions. Probably wear rate of the ZY5/L sample in water shows a stronger increase when higher pressures, longer sliding distances or higher sliding speeds are used.

4 Conclusions

The influence of ceria on tribological properties of Y-TZP were investigated. Therefore two types of nanostructured TZP ceramics, ZY5 (95 mole % ZrO_2 and 5 mole % $YO_{1.5}$) and ZY4Ce4 (92 mole % ZrO_2, 4 mole % $YO_{1.5}$, and 4 mole % CeO_2). From each type of powder two types of compacts are prepared with different grain sizes ($\pm$0·2 μm and $\pm$0·5 μm).

1. The ageing resistance of Y-TZP can strongly be improved by doping with ceria or decreasing the grain size. No ageing degradation under hydrothermal conditions occurs in ZY5 with a small grain size of $\pm$0·2 μm, but phase transformation is observed for the ZY5 compact with a grain size of 0·5 μm. No ageing degradation is observed for the ZY4Ce4 compacts, independent of grain size.
2. Both ZY5 and ZY4Ce4 samples with a grain size of $\pm$0·2 μm and a relative density of 95% almost show the same wear results after testing in dry nitrogen. Surface fatigue with cracks, caused by large shear stresses, and plastic deformation are the predominant wear mechanisms. For samples with a grain size of 0·50 μm, the wear rate of ZY5 compact is smaller than ZY4Ce4 compact. In this case surface fatigue is also the predominant mechanism but also grain pull out, abrasive wear and plastic deformation are observed as wear mechanisms.
3. Aqueous testing is entirely performed in the boundary lubricated regime. Due to this lubrication both friction coefficient and specific wear rate are strongly reduced. Only for ZY5 with a grain size of 0·5 μm phase transformation is observed. However, this does not influence the wear rate. Grain pull out is dominant in all samples tested in water while abrasive wear is also observed for the large grained samples. Grain pull out is enhanced by increasing the grain size of the TZP plates. At more extreme tribological conditions a phase transformation during wear in water can be detrimental.
4. Both wear rate and roughness of the SiC ball are related to those of the TZP counterparts.

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