DEVELOPMENT OF SURFACE-MODIFIED ALUMINA CERAMIC FOR BEARING COMPONENTS IN LIQUID MEDIA

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SUMMARY
Alumina ceramic was surface modified by remelting and alloying with pure zirconia and zirconia containing additions of SiO2 or Y2O3 using a high power CO2 laser. Tribological properties of the obtained multiphase ceramics were studied under oscillating sliding contact against alumina balls in the presence of distilled water, aqueous hydrochloric solution (HCl) and caustic soda (NaOH) as interfacial media and compared to those of a commercially available monolithic alumina ceramic. The results showed that friction coefficient of the tested sliding pairs were substantially lower in aggressive media than in distilled water. However, the lowest amount of linear wear was measured in the presence of distilled water. Compared to the monolithic alumina ceramic, the laser modified ceramics resulted in substantially higher wear resistance. Hence, surface modification can be very effective in improving oscillating sliding contact under boundary lubrication with liquid media.

Keywords: alumina; multiphase ceramic; surface modification; liquid media; wear resistance

1 INTRODUCTION
Advanced alumina ceramic is of increasing interest for wear components in liquid media, e.g. sliding bearings or seal rings in pumps for the chemical industry. These ceramic materials are qualified for such applications owing to their unique combination of low density, high stiffness and hardness, temperature stability and last but not least high corrosion resistance. However, inherent brittleness and lack of defect tolerance due to low fracture toughness and low thermal shock resistance can result in severe problems under high mechanical and/or tribological loads. The tribological behaviour of alumina at high loads is characterised by a transition from mild to severe wear, owing to a change of mechanism from predominantly tribochemical reaction to surface damage by microfracture. This wear transition is influenced not only by environmental (e.g. temperature, humidity, liquid media) and operating (e.g. sliding speed, load) conditions but also by microstructural parameters [1 - 6]. Improved tribological properties of alumina can be expected by microstructural modifications resulting in multiphase materials with enhanced fracture toughness [3].

Considering, that all tribologically induced interactions between two solids mated in sliding contact are concentrated on a relatively thin surface zone, it may be sufficient and economical to modify the microstructure for improved tribological performance in a surface zone of a few hundred micrometers in thickness only. It has been shown in recent studies that laser surface modification by remelting or embedding second phases can result in reduced friction coefficient and wear rate of oxide ceramics [7 - 10].

The aim of this work was to study the tribological behaviour of multiphase alumina ceramics produced by laser induced surface remelting and alloying of a commercially available monolithic alumina. Friction and wear of the ceramics were tested under oscillating sliding wear conditions with distilled water, aqueous hydrochloric solution (HCl) and caustic soda (NaOH) as interfacial media and compared to that of a dense monolithic alumina ceramic.

2 MATERIALS AND EXPERIMENTAL METHODS
Laser surface modification was carried out using a commercially available alumina (Al24, Friatec) with less than 5 vol% of open porosity (Table 1). The ceramic substrates were coated by a suspension consisting of isopropyl alcohol and different powders or powder mixtures such as ZrO2, ZrO2 + 5 mol% SiO2, ZrO2 + 5 mol% Y2O3 and 3Y-TZP (ZrO2, partially stabilised with 3 mol% Y2O3) (Table 2). After drying of the precoatings, the thickness was controlled and adjusted to 100 µm or 200 µm by removing excess powder. The precoated specimens were heated up to 1500 °C and laser remelting was carried out within an argon atmosphere using a CO2 laser at an average laser power of about 200 W. A beam integrator was used to generate a rectangular beam cross section of 1 x 6 mm² (Fig. 1a).

<table>
<thead>
<tr>
<th>Material</th>
<th>Al23</th>
<th>F99.7 (Ball)</th>
<th>Al24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average grain size (µm)</td>
<td>6.5</td>
<td>9</td>
<td>30</td>
</tr>
<tr>
<td>Hardness HV500</td>
<td>2030</td>
<td>1800</td>
<td>1900</td>
</tr>
<tr>
<td>Fracture toughness KIC (MPa m1/2)</td>
<td>3.4</td>
<td>3 - 4</td>
<td>&lt; 3</td>
</tr>
</tbody>
</table>

Table 1: Materials designation and microstructural parameters of the monolithic alumina ceramics.

More detailed information about the process of laser surface modification is given elsewhere [11]. Microstructures of the modified surfaces were
characterised using standard ceramographic techniques and scanning electron microscopy (SEM).

<table>
<thead>
<tr>
<th>Materials designation</th>
<th>Powder compounds of the precoating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al24Z</td>
<td>ZrO2</td>
</tr>
<tr>
<td>Al24ZS</td>
<td>ZrO2 + 5 mol% SiO2</td>
</tr>
<tr>
<td>Al24ZY</td>
<td>ZrO2 + 5 mol% Y2O3</td>
</tr>
<tr>
<td>Al24TZP</td>
<td>3Y-TZP</td>
</tr>
</tbody>
</table>

Table 2: Materials designation and additives of the surface modified alumina ceramic Al24.

Tribological properties of the laser modified ceramics were measured using a ball-on-block tribometer (Fig. 1c, Optimol SRV) under lubricated oscillating sliding contact at room temperature. Distilled water, 10% aqueous hydrochloric solution (HCl) and 10% caustic soda (NaOH) were used as interfacial media. The concentrations of the aqueous solutions are related to the value of 100% for concentrated HCl (37% HCl according to the chemical terminology) and saturated NaOH solution (at the temperature of 20°C). The tribological tests were run at a normal load of 40 N, an oscillating frequency of 20 Hz and a stroke of 0.5 mm, which resulted in an average sliding speed of 0.02 m/s. The total length of wear path was 144 m after a testing time of 2 hours. The alumina balls (F99.7, Ø 10 mm, Friatec) used as counterbodies were polished to a surface roughness of $R_s \leq 0.1 \mu m$. Before the tribological tests all block specimens were ground using a diamond wheel with a grit size of 25 µm. This resulted in an average surface roughness $R_s = 0.6 \mu m$ on the monolithic alumina Al23 used as reference material in the tribological tests and in a surface roughness $R_s = 0.3 \mu m$ on the laser modified ceramics. The grinding procedure led to a surface removal of about 150 to 200 µm in thickness. Friction coefficient and total amount of linear wear $W_t$ (sum of ball and block) were continuously measured and recorded during each test. In addition, amount of linear wear $W_t^*$ was separately determined for balls and blocks from surface profiles recorded with a profilometer after the tests. The reported friction coefficients and amounts of linear wear are average values of at least two individual tests.

![Figure 1: (a) Experimental set-up for laser treatment, (b) scanning electron micrograph (SEM) of a cross-section through a surface modified ceramic and (c) tribological system (ball-on-block) used in oscillating sliding wear tests.](image)

![Figure 2: SEM of cross-sections through the commercial ceramics (a) Al23, (b) F99.7 (ball) and the laser surface modified ceramics (c) Al24Z, (d) Al24ZS, (e) Al24ZY and (f) Al24TZP.](image)
3 RESULTS

Microstructures of the commercially available monolithic alumina ceramics Al23 and F99.7 which were used for reference (Al23) and as counterbodies (F99.7) in the tribological tests are shown in Fig. 2a and 2b. Both ceramics showed some closed porosity. According to Table 1, the average grain size of Al23 was 6.5 µm whereas that of F99.7 was about 9 µm. Laser treatment led to dense, multiphase surface layers with a thickness between 400 and 500 µm, depending on the alloying additions (Fig. 1b). The laser modified microstructures were characterised by a matrix of alumina crystallites and a fine lamellar eutectic phase which occurred along the grain boundaries of the alumina crystallites (Fig. 2c - 2f). This reaction phase consisted mainly of ZrO2 and Al2O3 and its amount was measured to about 20 vol%. The average size of the alumina crystallites was reduced within the modified surface zone up to a factor of 3 compared to the substrate ceramic Al24 (Table 1). All laser modified ceramics showed locally columnar grains with lengths up to about 300 µm which were predominantly orientated perpendicular to the surface (Fig. 1b). Due to thermally induced stresses during cooling, the modified surfaces of the ceramics Al24Z, Al24ZY and Al24TZP showed a tendency to form crack networks. In the modified ceramic Al24ZS containing ZrO2 and SiO2 additions the crack density was markedly reduced.

Figure 3 shows friction coefficient and total amount of linear wear measured on the reference ceramic Al23 and the laser modified ceramic Al24TZP mated against the alumina balls (F99.7) as a function of the time of testing. Under lubrication by distilled water the friction coefficient of the sliding pair F99.7/Al23 increased immediately after starting the test to a maximum value of about 0.45 (Fig. 3a). After a sliding distance of about 14.4 m (t = 12 min) the friction coefficient decreased to a value of 0.31 and increased again with prolonged testing time to 0.35 at the end of the test. A substantially smaller quasistationary friction coefficient of about 0.2 was measured with the F99.7/Al23 sliding pairs lubricated by NaOH or HCl (Fig. 3a). The highest amount of linear wear showed the sliding pair lubricated with HCl. After a sliding distance of 144 m (120 min) the amount of linear wear was 39 µm compared to 24 µm and 11 µm with the sliding pairs lubricated by NaOH and distilled water, respectively (Fig. 3c). According to Fig. 3b and 3d the sliding pair F99.7/Al24TZP showed comparable values of the quasistationary friction coefficient in all liquid media but substantially smaller amount of linear wear than the reference sliding pair F99.7/Al23. Under lubrication by HCl or NaOH the sliding pairs of the modified ceramic Al24TZP exhibited an about 40 % smaller amount of linear wear than the sliding pairs of the reference ceramic Al23 (Fig. 3d).
Fig. 4 summarises the quasistationary values of friction coefficient and the amount of linear wear of the different pairs after a sliding distance of 144 m. The highest values of the friction coefficient between 0.35 and 0.5 were measured on sliding pairs under lubrication by water (Fig. 4a). Substantially smaller values of the friction coefficient in the range of 0.2 were obtained during tests in NaOH or HCl. The highest amounts of linear wear of both balls and blocks were determined under lubrication by HCl (Fig. 4b). The smallest amounts of linear wear occurred in distilled water. For these sliding pairs the total amount of linear wear was between 9 and 11 µm and therefore about the factor of 3 to 4 smaller compared to the tests in HCl. In the presence of water the wear of the alumina balls was comparable independent whether mated with the monolithic or the lasermodified ceramics. In aggressive media such as HCl and NaOH the wear of the balls was between 30 to 50 % lower when mated with the modified ceramics.

Figure 5 shows scanning electron micrographs of worn surfaces of the ceramics Al23 and Al24TZP after sliding 144 m in the presence of distilled water, NaOH and HCl, respectively. The reference ceramic Al23 displayed small grooves and a lot of grain pull-outs on the worn surface after sliding in water. The number of grain pull-outs on the worn surface of the ceramic Al23 was substantially smaller after the tests in the presence of NaOH or HCl (Fig. 5b and 5c). Independent of the interfacial media the laser modified ceramic Al24TZP showed a smooth surface with small grooves but no grain pull-outs (Fig. 5d - f) after 144 of sliding.

4 DISCUSSION

The experimental results showed that CO2 laser irradiation can be effectively used for surface modifying alumina by embedding zirconia with additions of SiO2 or Y2O3. The thickness of the multiphase surface layers ranged between 400 and 500 µm depending on the composition of the powder precoating. The composite microstructures contained about 20 vol% of second phases as reaction phase along the boundaries of the Al2O3 crystallites.

In the tribological tests all sliding pairs showed the highest values of friction coefficient in distilled water. In the presence of aggressive media such as HCl and NaOH, the friction coefficient was about 40 to 50 % lower than in distilled water. This behaviour could be explained by the higher concentration of OH- groups or H⁺ ions in the aggressive media which led to an increased formation of tribochemical reaction layers on the ceramic surfaces. Soft aluminium hydroxide films can effectively reduce friction owing to their low shear strength [4, 12]. The wear rate of the sliding pairs was mainly determined by the formation and dissolution of the reaction films in the aqueous solutions. Because of the higher dissolution rate in aggressive media, linear wear was greater in the presence of HCl or NaOH than in distilled water [4 - 6]. In literature it was reported that the aggressive media could lead to a greater wear rate due to stress corrosion cracking [5, 6]. Compared to the monolithic alumina Al23, the laser modified ceramics showed up to 40 % lower amounts of linear wear. This was explained by microstructural effects due to the laser treatment of the alumina ceramic. Embedding of a second phase like zirconia resulted in lower hardness and Young’s modulus and therefore in reduced local contact pressure by increasing the true area of contact [10]. Spalling of individual grains, which was an important wear mechanism with the monolithic alumina (Fig. 5a - 5c) could be effectively hindered by the reaction phase at the grain boundaries and also by the preferred orientation of the alumina crystallites perpendicularly to the wearing surface [3, 7, 10]. Recent studies on conventionally sintered ZTA (Al2O3-ZrO2) materials attributed an increased wear resistance under lubricated and unlubricated sliding mainly to increased fracture toughness and lower grain size of these materials compared to monolithic alumina [13 - 15].
Figure 5: SEM of surfaces of (a, b, c) Al23 and (d, e, f) Al24TZP worn during oscillating sliding contact against AlO,
balls under feeding of (a, d) distilled water, (b, e) aqueous caustic soda and (c, f) hydrochloric solutions.

An increased wear resistance was also reported [7, 9] with an alumina ceramic laser alloyed by additions of
agreement with other studies on the tribological
properties of Al2O3-ZrO2 ceramics, no preferred wear of the
zirconia phase was observed in the present study
[13 - 15].

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