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Wear behaviour of single phase and composite sialon ceramics stabilized with Y_2O_3 and Lu_2O_3

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Abstract

The wear properties of single phase α and two phase α/β composite sialon ceramics sintered with both yttria and lutetia have been studied under dry conditions using block on ring wear tests. Under high load conditions, where microcracking and grain pullout are the predominant wear modes the composite materials showed better wear properties than the single phase materials. Under low load wear, where tribochemical phenomena are thought to provide a major wear mechanism, the single phase materials showed better wear properties than the composites. Under these conditions there was a large effect of the stabilizing cation, with the Lu stabilized sample having a wear volume an order of magnitude lower than that of the Y stabilized one. The improved wear resistance of the Lu stabilized sample is attributed to the higher thermal stability of the sialon phase sintered with smaller cations and the more refractory nature of the residual grain boundary phase.

Keywords: Composites; Mechanical Properties; Sialon; Wear resistance

1. Introduction

In silicon nitride materials the oxide additives used to aid sintering result in materials containing a significant amount of grain boundary phase, typically around 10 wt.%, and the properties of the materials are therefore determined to a large extent by the properties of this phase. Additives of more refractory oxides such as Yb_2O_3 and Lu_2O_3 have been shown to improve mechanical properties, particularly at high temperature.[1] Incorporating Al and O into a Si_3N_4 matrix results in the family of solid solution ceramics known as SiAlONs. The two major phases are α and β, which are isostructural with α and β Si_3N_4 and which are given by the formulae $RE_xSi_{12\text{-}(m+n)}Al_{(m+n)}O_nN_{16\text{-}n}$, and $Si_{6\text{-}z}Al_zO_zN_{8\text{-}z}$ respectively. β SiAlON is formed through simultaneous substitution of z (Si–N) by z (Al–O) bonds. In the α phase, where the valency discrepancy arising from the substitution of m (Si–N) bonds by (Al–N) and n (Si–N) being replaced by (Al–O) is compensated for by the incorporation of the rare earth metal ion RE $^{p+}$, the extent of the incorporation of this ion, x, given by $x=m/p$, results in the possibility of sintering via a transient liquid phase route resulting in ceramics with a reduced amount of intergranular phase.[2] Yttria stabilized sialons are probably the most well studied although a range of RE can be incorporated in the α structure; the stability of the α phase has been shown to increase with decreasing cation radius.[3] Although to the authors' knowledge, Lu_2O_3 has never been employed as the stabilizing cation in α sialon ceramics, its use as a sintering aid in silicon nitride materials has been shown to improve both high temperature strength and strength retention following oxidation.[4,5]

In a recent account of the wear properties of yttria based sialon ceramics, it was shown that the wear behaviour depends significantly on the microstructure and chemical stability of the materials.[6] In this work, it was shown that under severe wear conditions, the wear properties of high β containing samples were much better than those of single phase α ones, due to the higher fracture toughness and the better resistance to the predominant wear mechanisms of microcracking and grain pullout. However, under mild wear conditions, the situation was reversed with the single phase materials

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showing better wear resistance. This was attributed to the reduced amount of grain boundary phase and the improved chemical stability, important where the wear mechanism is one of tribo-chemically assisted wear. In this paper we extend the research to investigate the effect of the rare earth element (RE) employed in stabilizing the sialon phase, as this has a significant role in determining the thermal stability of the material, and as such is expected to affect the wear properties, particularly under tribochemical type wear conditions.

2. Experimental

2.1. Sample preparation

In RE-α-Sialons where the RE cation valence is 3^+, the nominal composition of the material is given by the formula $RE_{m/3}\ Si_{12-(m+n)}Al_{m+n}\ O_n\ N_{16-n}$. Fig. 1 shows the position of the α sialon plane in the RE-Si-Al–O-N Janecke prism and the starting compositions employed in the current work. For each of the RE systems, a single phase α-sialon material ($m=1.1$, $n=1.1$) and a two phase α sialon/β Si_3N_4 composite ($m=0.5$, $n=0.25$) was produced by mixing appropriate amounts of α-Si_3N_4 (E-10 grade, Ube Industries, Ltd., Japan), Al_2O_3 (AKP-50, Sumitomo Chemical Co., Ltd., Japan), AlN (F grade, Tokuyama Co. Ltd, Japan) and RE_2O_3 (Y_2O_3; RU-P, Lu_2O_3; 99.9%, Shin-Etsu Chemical Co., Ltd., Japan) in methanol using a Si_3N_4 pot and Si_3N_4 balls. The slurry was dried, and then passed through 125 mesh. The powders were hot-pressed at 1950 °C for 2 h with an applied pressure of 40 MPa in a 0.9MPa N_2 atmosphere.

2.2. Characterization

Phase identification was carried out by X-ray diffractometry, and the fracture surfaces of the samples following sintering were observed by scanning electron microscopy, SEM, (JSM-6340F, Jeol Ltd., Japan). TEM analysis was carried out using a JEM 400OEX, Jeol Ltd., Japan.

For mechanical property measurements, test bars with dimensions of 3 × 4 × 40 mm were machined from the sintered specimens and polished on the tensile face. Additional samples for Block-on-Ring tests were machined to a size of 3 × 4 × 1.5 mm thickness, Strength measurements were carried out by four-point bend with inner and outer spans of 10 mm and 30 mm respectively, and a crosshead speed of 0.5 mm min^{-1}. Vickers hardness was determined under a load of 98 N, and fracture toughness (K_{IC}) was determined by the indentation-fracture (IF) method under the same load. In all experiments, the samples were tested on the face normal to the hot pressing direction, and the results are given as the average of 5 tests.

Block-on-Ring tests were carried out under non-lubricated conditions using the equipment described in a previous paper.[6] The sialon samples were employed as the blocks, and the ring was a commercially available silicon nitride material (SN235P, Kyocera, Japan). The surface roughness of both the Si_3N_4 ring and the sialon specimens was prepared under Rz 0.1μm. Temperature

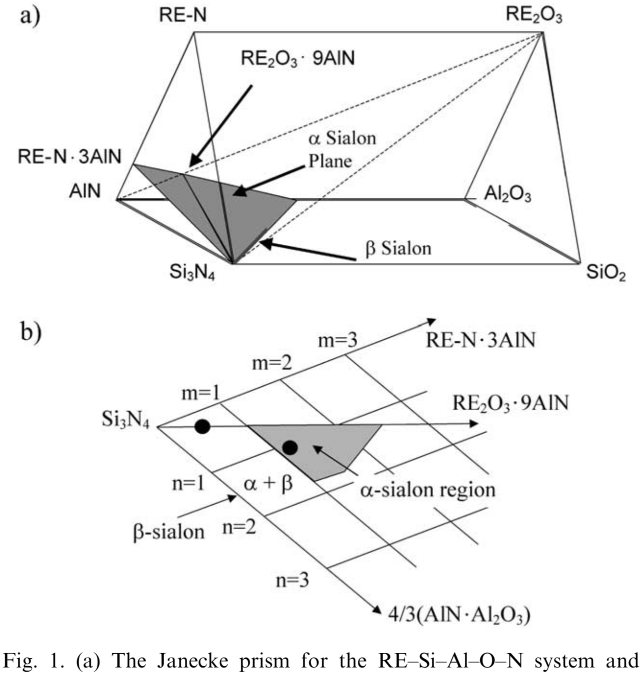

Fig. 1. (a) The Janecke prism for the RE–Si–Al–O–N system and (b) the starting compositions of the materials in the α-sialon plane.

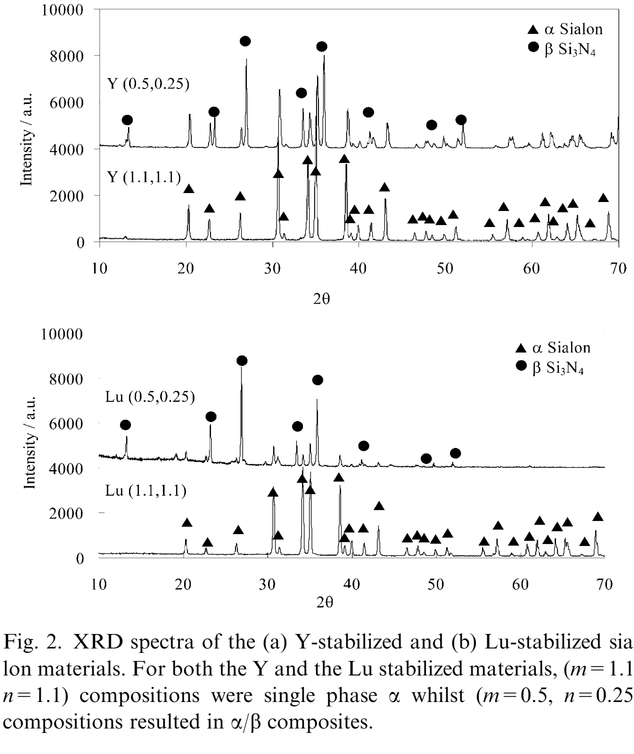

Fig. 2. XRD spectra of the (a) Y-stabilized and (b) Lu-stabilized sialon materials. For both the Y and the Lu stabilized materials, ($m=1.1$, $n=1.1$) compositions were single phase α whilst ($m=0.5$, $n=0.25$) compositions resulted in α/β composites.

and humidity were kept constant at 25±3 °C, 25±2%RH. Sliding speed and distance were kept constant at 0.15 m/s and 75 m, respectively, and the tests were conducted with normal loads ranging from 5 to 90N. The sectional worn area of the sialon block was measured in nine equidistant positions in the direction parallel to the sliding direction, and the worn volume of the block specimen, V, was calculated by integration of the sectional worn area.

3. Results and discussion

XRD spectra shown in Fig. 2 revealed that both of the ($m=1.1$, $n=1.1$) compositions resulted in single phase α sialon, whilst for the ($m=0.5$,$n=0.25$) compositions β Si_3N_4 was also observed. The microstructures of the materials are shown in Fig. 3. The single phase α materials, Y(1.1,1.1) and Lu(1.1,1.1), both showed equiaxed microstructures with similar grain size of 1 – 2 μm. For the composite materials, the anisotropic growth rates of the β Si_3N_4 crystal resulted in the presence of elongated β grains in a fine-grained α matrix. TEM micrographs of the Lu-stabilized materials are shown in Fig. 4. For the ($m=1.1$, $n=1.1$) composition, the incorporation of the sintering elements in to the sialon structure resulted in materials with a reduced amount of grain boundary phase when compared to the composite material. However, there were small amounts of residual boundary phase observed at triple junctions, and lattice parameter measurements calculated from XRD data indicated that the actual composition, determined using the formula reported by Sun et al.,[7] was $m=1.00$ and $n=0.97$, that is the grains were slightly rich in Si and N and indicating that not all of the additives had entered into the sialon structure. Supporting this analysis, EDX analysis of the triple point phase, shown in Fig. 5, indicated that it was rich in Lu and also

Table 1
Properties of the single phase α sialon and two phase α / β ceramics

Sample	Phase structure	Hardness GPa	Toughness MPa.m$^{1/2}$	Strength MPa
Y (1.1,1.1)	α	18.7	2.45	402
Y (0.5,0.25)	α + β	17.6	5.40	879
Lu (1.1,1.1)	α	19.3	2.55	392
Lu (0.5,0.25)	α + β	18.2	4.92	836

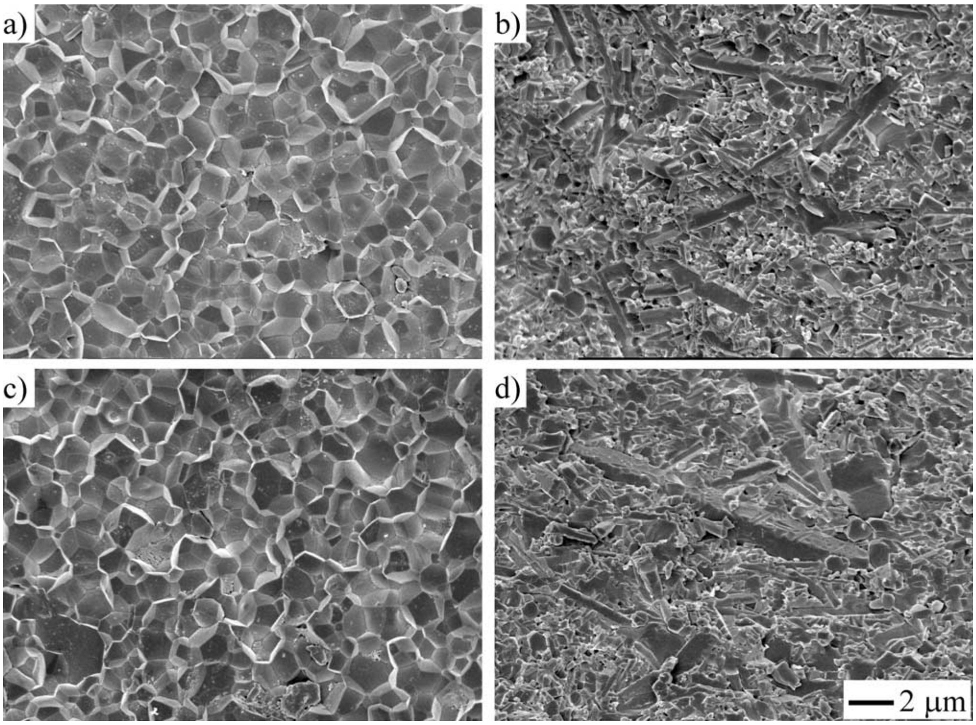

Fig. 3. Microstructures of (a) Y(1.1,1.1), (b) Y(0.5,0.25) (c) Lu(1.1,1.1) and (d) Lu(0.5,0.25). The single phase materials possessed equiaxed microstructures (a and c) whilst elongated β grains were observed in the composites (b and d).

contained Si, N and O. Work on Lu-stabilzed Si_3N_4 has shown that both J phase, $Lu_4Si_2O_7N_2$, and Lu_2SiO_5 are observed as boundary phases.[8] Similar results have been observed for the Y-stabilized sialons, however, it is recognised that this discussion is only qualitative and more detailed research into the nature of the grain boundary phase in all of these materials is currently being undertaken and will be reported separately.

The room temperature mechanical properties of the sintered samples are given in Table 1. The single phase materials showed similar values for the two sialons, with hardness of around 19 GPa, fracture toughness of around 2.5 MPa.m$^{1/2}$ and bending strengths of around 400 MPa. For the composite materials there was a slight decrease in hardness when compared to the single phase sialons, but the presence of the elongated β grains resulted in an increase in fracture toughness and strength to values around twice those of the comparable single phase material.

The wear volumes of the materials subjected to both low and high load block on ring wear tests are shown in Fig. 6. Under high load conditions (Fig. 6a) for both the Y- and Lu- stabilized samples the two phase materials showed lower wear volumes than the equivalent single phase material. The worn surfaces of the samples following high load block on ring tests are shown in Fig. 7. The surfaces were covered with large amounts of crushed debris and in areas where this debris had been removed, microstructural features akin to fracture surfaces were exposed. These microstructural features indicate that the predominant wear mechanism under these conditions was one of mechanical wear. In Si_3N_4 based materials it has been shown that under conditions where the wear conditions become more severe, such as high stress or high load conditions, the predominant wear mode is one where wear occurs by the propagation of cracks along the grain boundaries leading to microfracture.[9] Such intergranular cracking can lead to the ‘‘pulling out’’ or ‘‘dropping’’ of grains from the material surface.[10] Under this type of mechanical wear mode the mechanical properties of the material are thought to be more important than the chemical stability, and the better wear resistance of the composite materials is attributed to the higher fracture toughness, produced through the presence of elongated microstructures, being effective for resisting crack propagation through crack deflection and crack bridging effects. For the α samples, both samples had an equiaxed microstructure and similar mechanical properties, and under such mechanically dominated wear the wear rates were similar.

Worn surfaces of the materials following low load wear tests are shown in Fig 8. The appearance of the

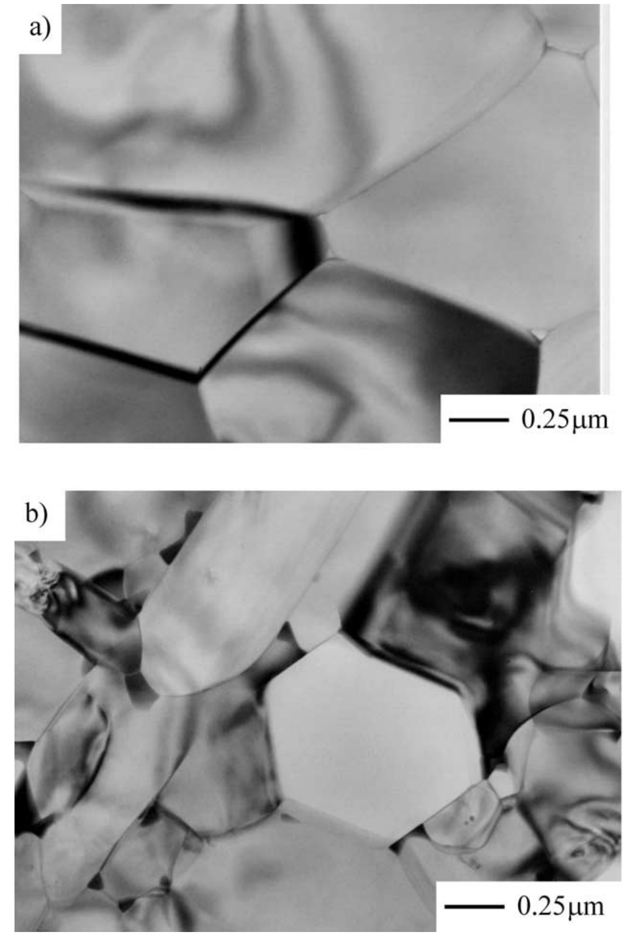

Fig. 4. TEM images of the Lu stabilized materials. The α sample (a) showed an equiaxed microstructure whilst the α/β composite (b) showed elongated β grains in a fine-grained α matrix. The single phase α material showed very small pockets of residual grain boundary phase at triple junctions whereas the amount of grain boundary phase in the composite was qualitatively much larger.

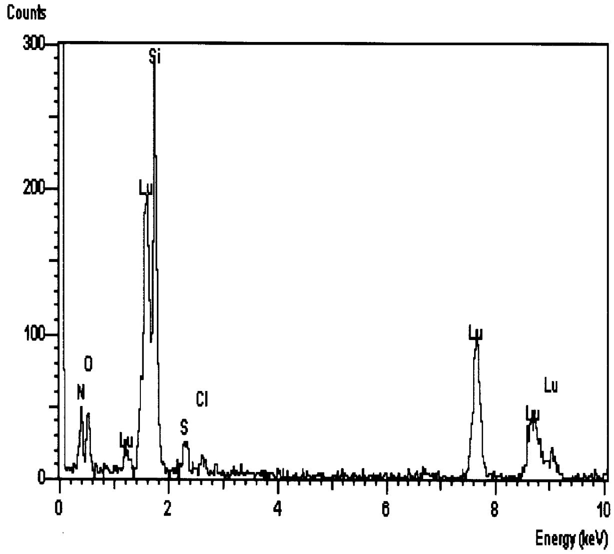

Fig. 5. EDX spectrum taken from one of the triple junctions of the Lu (1.1,1.1). A high concentration of Lu was observed in these small residual pockets.

surfaces was significantly different to those observed under high loads. Under these conditions, the surfaces were smooth with no obvious signs of the mechanical type wear described above. Grain boundary phase removal was observed and it is thought that tribochemical wear was the main wear mechanism. In silicon nitride ceramics tribochemical reactions between the sliding surface and water vapour in the air, stimulated by friction, result in the oxidation of the surface and the formation of an amorphous $Si(OH)_4$ layer.[11]

The wear volumes of the materials under these conditions (Fig. 6b) showed that for both types of sialon, the single phase materials showed lower wear volumes than the corresponding composite, although the difference was not so large in the Y-stabilized materials as it was in those sintered with Lu. In previous work it was suggested that the improved wear resistance of single phase materials under tribochemical wear was due to the reduced amount of grain boundary phase and better oxidation resistance.[6]

In this present work, there was a large effect of the stabilizing cation within the single phase materials under low loads, with the wear volume of the Lu stabilized α sialon being an order of magnitude lower than that of the Y stabilized one. Under this type of tribochemical type wear, and with grain boundary removal being one of the major modes of material removal, the thermal stability of the sialon grains and the properties of the residual grain boundary glass phase can be expected to have an influence on the overall wear behaviour. Indeed under these conditions, although the amount of grain boundary phase was higher in the composites than in the single phase materials, the wear volume of the Lu-stabilized composite was lower than that of the Y-single

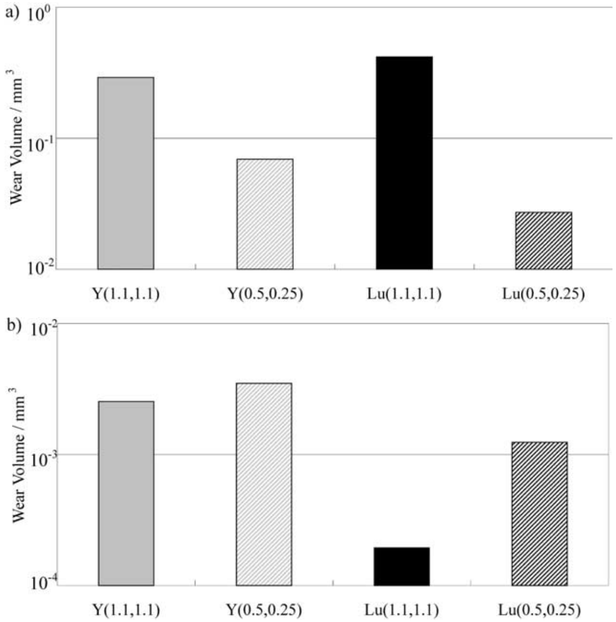

Fig. 6. Worn volumes of the samples following block on ring wear tests at loads of (a) 90N and (b) 5N. Under high loads the composites show better wear resistance, but the single phase materials show lower wear under low loads. There was a large effect of cation species under low load, tribochemical type wear.

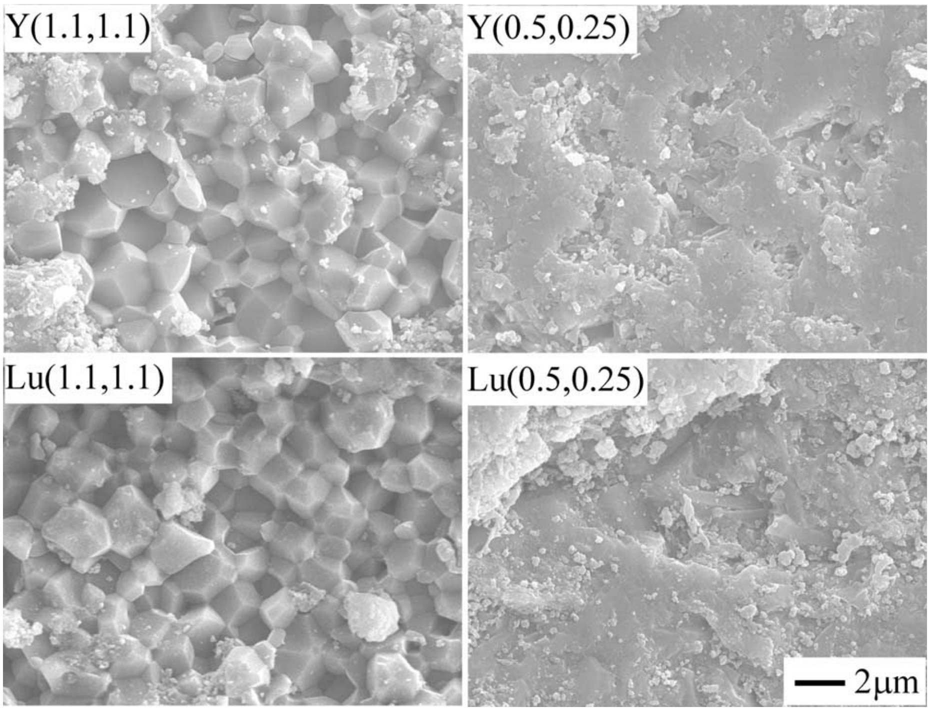

Fig. 7. Worn surfaces following block on ring wear tests at 90N. Mechanical wear resulted in grain pullout, particularly noticeable for the single phase α materials (a and c).

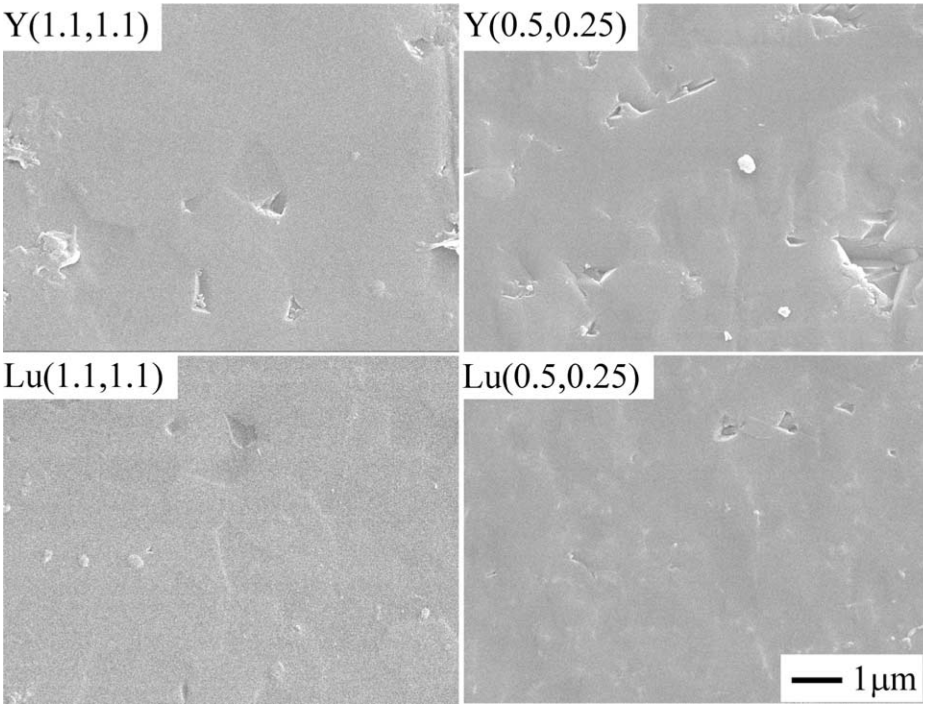

Fig. 8. Worn surfaces of the samples following 5N block on ring wear tests. The worn surfaces were smooth with areas of grain boundary removal being observed.

phase material, indicating that not only the amount of grain boundary phase, but also the properties of both this grain boundary phase and the sialon grains themselves play an important role in the resistance to tribochemical type wear.

Work on silicon nitride ceramics sintered with different rare earth disilicate additions has shown that rare earths with smaller ionic radius resulted in improved oxidation resistance.[1,12] The same trend of improved oxidation resistance with decreasing cation size has also been reported for α sialon ceramics [13] and rare earth silicon oxynitride glasses.[14] In addition to the improved oxidation resistance, a number of works on the properties of aluminosilicate, RE–Si–O–N and RE–Si–Al–O-N glasses has shown that for smaller rare earths properties such as hardness and glass softening and glass transition temperatures increase.[15–17] This has been attributed to the fact that the cationic field strength increases with decreasing cationic radius and that this leads to a stronger glass network. Numerous works on the stability and properties of different rare earth stabilized sialons have also shown that materials stabilized with cations of a smaller ionic radius have a greater stability at high temperature.[18,19] It is considered that this improved thermal stability of the Lu-stabilized sialon, in addition to the presence of a more refractory grain boundary phase with smaller ionic radius [1,8] is responsible for the improved wear resistance of these materials compared to those stabilized with yttrium under tribochemical type wear.

4. Conclusions

Single phase α sialon and two phase α sialon/β Si_3N_4 materials have been produced using Y and Lu as the stabilizing cation in the sialon phase, and their wear properties assessed under dry sliding conditions. Under high loads where mechanical type wear was the predominant wear mechanism the better mechanical properties of the composites afforded by the presence of elongated β grains resulted in lower wear than the single phase materials.

However under low loads where tribochemical reactions are thought to be one of the dominant wear mechanisms, the single phase materials showed better wear resistance. Under these conditions there was a large effect of the cation species, with the sample stabilized with the Lu cation having a wear volume an order of magnitude lower than that of the Y stabilized material. This is attributed to greater thermal stability and a more refractory grain boundary phase arising due to the smaller cationic radius of the stabilizing element.

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