Sliding wear behavior of submicron-grained alumina in biological environment

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Abstract: Sliding wear behavior of sintered alumina with grain sizes between 0.45 and 4 μm was studied in bovine serum environment with unidirectional pin-on-disc wear testing machine. Submicron grained alumina of average grain size of G = 0.45 μm exhibits lowest wear factor among the others. It was found that grain pull out or localized grain dislodgement caused by coalescence of grain boundary microcracks is the basic wear mechanism of submicron grained alumina though the extent of cracking and pull-out was substantially less than that with higher grained material. However, in few cases, some areas where substantial volume of material was removed following pull-out of cluster of grains have also been observed. © 2007 Wiley Periodicals, Inc. J Biomed Mater Res 83A: 257–262, 2007

Key words: orthopedic implant; friction; grain pull-out; microcracking; grain boundary toughness

INTRODUCTION

Zirconia, particularly 3Y-TZP, because of its high strength, high toughness, and moderate hardness, has been thought to be an advanced bioinert material and is claimed to possess an edge over conventional alumina. However, zirconia has a well-known problem of aging; particularly, during steam sterilization of the orthopedic implants ($\sim$134°C, 2 bars); the accelerated transformation from tetragonal to monoclinic phase of zirconia is often reported to give rise to micro-cracks at the implant surface and it was proved to be detrimental to the long term performance of the implanted hip prosthesis.[1–3] Alumina is free from this aging problem. Furthermore in recent time, with the growing availability of nanosized commercial powders coupled with advanced processing routes, submicron grained alumina with high strength,[4] high hardness,[4,5] and moderately high toughness[6] has been developed. These favorable properties make this new generation fine-grained alumina a potential substitute to 3Y-TZP in arthroplasty. In recent years, number of processing routes ranging from hot iso-static pressing (HIP)[7] to pressure filtration or gel casting[4,8,9] have been evolved for generation of this high density, high hardness sub-micron-grained alumina. Even slip casting, an age-old processing technique used in ceramic industry, has also been exploited to produce alumina of submicron grain size by using very fine starting powder and ensuring formation of agglomerate-free slip.[10] However, the long term mechanical performance of this new grade of alumina, particularly its wear and fatigue property, has not been characterized in detail so far. In the specific area of wear, there is still lack of experimental data. In recent past, Krell[11] have studied the wear resistance of this newly developed sub-micron-grained alumina and tried to correlate it with the mechanical properties as well as some of the extrinsic parameters. Krell and Klaffke[12] in another paper have reported the effect of humidity on the role of microstructural features (e.g. grain boundary stability) in controlling fretting wear. But the volume of data generated so far is still very small and the understanding regarding the wear mechanisms is far from being complete. Moreover, till date, neither the effect of biological environment nor that of simulating stresses acting on artificial joints on the tribo-performance of this new grade of alumina has been reported in details. So despite the wealth of literature on the wear of alumina,[13–17] there is specific need and scope to de-

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velop a precise and clear understanding regarding the micromechanics of sliding wear for this newly available, sub-micron-grained alumina in biological fluid. In the present study, sliding wear behavior of submicron alumina with average grain size of 0.45 μm was investigated and compared with different higher grained alumina (0.95 and 4 μm) in bovine serum environment.

MATERIALS AND METHODS

Submicron grained alumina was prepared by slip casting of commercially available α-alumina powder (TM DAR, Taimei Chemical, Japan) with a mean particle size of 170 nm. The slip was prepared according to the process described by Lim et al.[10] The powder was dispersed in HCl solution with suitably controlled pH value of 2.4. The optimized pH value was confirmed by a series of sedimentation experiments. A solid loading of 30 vol % was used to prepare the samples. Soft agglomerates were broken by ultrasonic agitation. The pH value was kept constant throughout the process by adding additional HCl whenever required. The slip was kept unstirred for 24 h to allow the hard agglomerates to settle down. After 24 h, the sediment (i.e. hard agglomerates) was eliminated by carefully separating the supernatant. The slip was poured in a gypsum mould and the cast samples were air-dried. The air-dried samples were further dried up to 120°C in an air-oven by increasing the temperature at a rate of 10°C/day and subsequently prefired at 800°C for 1 h to obtain a prefired density of >64% of the theoretical density. Prefired samples were then given to a shape of rectangular bar by carefully hand-grinding with sand paper. After optimizing the suitable sintering temperature [Fig. 1], the prefired alumina bars were finally sintered at 1275°C for 1 h to obtain a relative density of >99.8%. The sintered bars were mounted in an araldite based polymer and subsequently given to a shape of cylinder of 3.25 mm diameter with the help of a cylindrical grinding machine. A 45° beveled cut at the tip of the pin was made by using a surface grinding machine and polished to a roughness value of $R_a < 0.05$ μm. The disc ($\phi = 150$ mm) with a central hole of 25 mm was also prepared through identical processing steps.

The microstructure of the polished sample was obtained by thermal etching at 1225°C for 30 min. Photographs of etched sample [Fig. 2(a)] were obtained by using a Scanning Electron Microscope (LEO 430i STEROSCAN, UK). The grain sizes were determined by linear interception: average grain size $G = 1.56 \times$ average linear intercept[18] and was found to be $G = 0.45$ μm. Samples were also prepared by cold isostatic pressing (~150 MPa) of the alumina powder followed by sintering at 1350 and 1600°C yielding grain sizes of 0.95 and 4 μm respectively [Fig. 2(b,c)] and for comparison, these samples too were used in the present wear study. Vicker's hardness and fracture toughness[19] of all the sintered samples were determined by indentation on polished sample (≈16.5 mm diameter × 2.2 mm thickness) at 50 N load.

Simple pin-on-disc unidirectional wear and friction testing machine (model no. TR 20L, manufactured by M/s

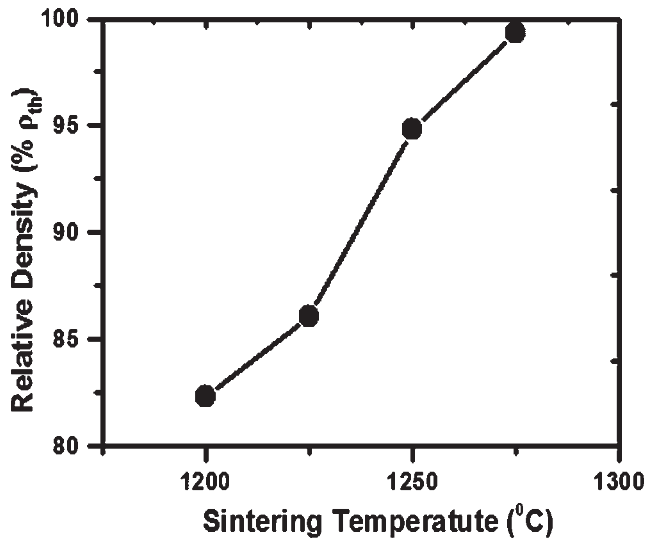

Figure 1. Change of relative density with sintering temperature for submicron grained (i.e. $G = 0.45$ μm) alumina made by slip casting.

Ducom, Bangalore, India) was used for this study. Each pin sample was ultrasonically cleaned and dried before and after the experiment. Volumetric wear of pin was calculated from gravimetric measurement. All the investigations were performed in 25% bovine calf serum (Harlan Sera-Lab, Loughborough, U.K.) diluted with double distilled water. 20 m*M* EDTA was added to the lubricant to minimize precipitation of calcium phosphate on to the contacting surface and 0.2 vol % sodium azide was used to retard bacterial degradation. Experiments were conducted with a sliding speed of 0.2 m/s under a constant rotational speed of 50 rpm of the disc. Each test was continued up to a sliding distance of 7.2 km with normal load of 10 N and 50 N. A flat-on-flat test geometry (i.e. conformal contact) was used for the whole set of experiments. The samples were weighed before and after the test on an electronic microbalance (METTLER TOLEDO, model no. AG 285) with an accuracy of 5 decimal places. Each experiment was repeated at least thrice to check the reproducibility of data.

RESULTS

Table I shows the density, Vicker's hardness and fracture toughness of all the alumina used in the present study. The coefficient of friction (μ) of different grain sized alumina is presented in Figure 3(a). It was found that the change of 'μ' within the selected range of grain sizes do not vary significantly. This observation is in agreement with most of the studies related to the grain size effect on alumina wear reported so far[12,15] where no definite correlation between grain size of alumina and coefficient of friction was noticed. However, only in the present study, to assess the suitability of the material for load bearing orthopedic application, a biological

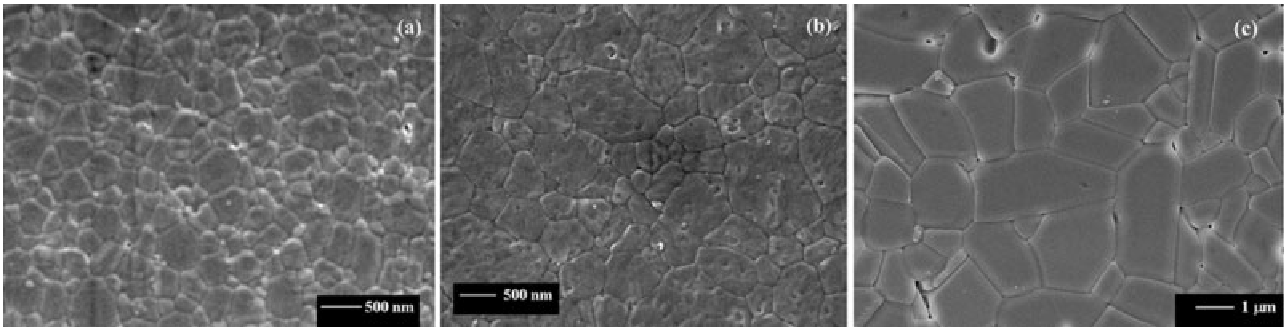

Figure 2. Microstructure of the alumina used for the present study with average grain size of (a) $G = 0.45$ μm, (b) $G = 0.95$ μm, (c) $G = 4$ μm.

environment was used whereas most of the reported study, experiments were conducted in dry condition[15,20–21] or in distilled water.[12] In the present work, the coefficient of friction remains more or less constant with sliding distance [Fig. 3(c)] throughout the experiment for all specimens except for the samples of submicron grained alumina where 'μ' shows a very small variation with sliding distance.

The wear factors of the alumina used in the present study shows a decreasing trend with decreasing grain size [Fig. 3(b)]. The average wear factor (W.F.) of five repeated experiments of submicron grained alumina (i.e. average W.F. $= 2.18 \times 10^{-7}$ mm^3/N m for $G = 0.45$ μm) was found to be almost half compared with the average wear factor of alumina of $G = 0.95$ μm (average W.F. $= 3.92 \times 10^{-7}$ mm^3/N m). Alumina with a grain size of 4 μm shows a much higher wear factor (W.F. $= 5.81 \times 10^{-7}$ mm^3/N m) compared to others. It is noteworthy that for all the experiments with submicron alumina, the wear factor of each individual experiment was always lower than the higher grained alumina. This consistency points at the superiority in wear resistance of the submicron grained alumina over the higher grained ones.

SEM micrographs of the worn surfaces of the test pin samples show that in bovine serum, grain boundary microcracking followed by grain pull-out is the dominant wear mechanism involved in alumina [Figs. 4–6]. Increase in grain size increases grain boundary micro-cracking as well as the severity of grain pull out. Figure 4(a–c) show worn out samples of all three grain sizes with maximum and identical load (50 N). From the figures, it is evident that with average grain size of 0.45 μm, the area of pull-out is less [Fig. 4(a)]. With the increase in grain size, more amount of grain dislodgement occurs. For average grain size of 4 μm, extent of pull-out is maximum [lFig. 4(c)].

There are clear evidences of grain boundary micro-cracks [Fig. 6(a–c), zone 'Q'] and their coalescence. Numbers of grains are clearly on the verge of being pulled out. The observation conforms well to the model proposed by Ajayi and Ludema[22,23] and Xu et al.[24] which suggests that generarion, growth, and coalescence of microcracks causes grain pull-out and subsequent wear loss in alumina. For submicron alumina ($G = 0.45$ μm), in one or two cases with higher loads, occasional removal of slightly larger volume of material, involving a small cluster of grains was also observed [Fig. 5 (b), zone 'P']. For bigger grained alumina, this feature [Fig. 6(c), zone P] was found more frequently.

TABLE I
Density, Vickers Hardness and Indentation Fracture Toughness (Test Load = 50 N) Data of Various Grained Alumina Used in the Present Study

Grain Size	4 (μm)	0.95 (μm)	0.45 (μm)
Density (gm/cc)	3.94	3.92	3.96
Vickers Hardness (GPa)	17.50	20.56	23.77
Indentation toughness (MPa m$^{-0.5}$)	3.21	3.25	3.28

DISCUSSION

In case of alumina, wear process is generally controlled by brittle fracture and fracture toughness plays an important role in wear resistance. Fracture toughness of polycrystalline alumina is reported to increase with increasing grain size because of more pronounced effect of bridging grains[25] that inhibits the fracture process. However, grain bridging is not so effective in the present case, as grain dislodgement and inter-granular micro-fracture are found to be the main processes controlling wear (Fig. 4) that occurs as a result of micro-crack propagation and their coalescence surrounding individual grains or group of grains. Hence, the macro-cracks from which K_{IC} values are measured do not resemble the type of small cracks as observed in the present set of worn out test samples. Therefore, the increased severity of wear with larger grains in comparison with

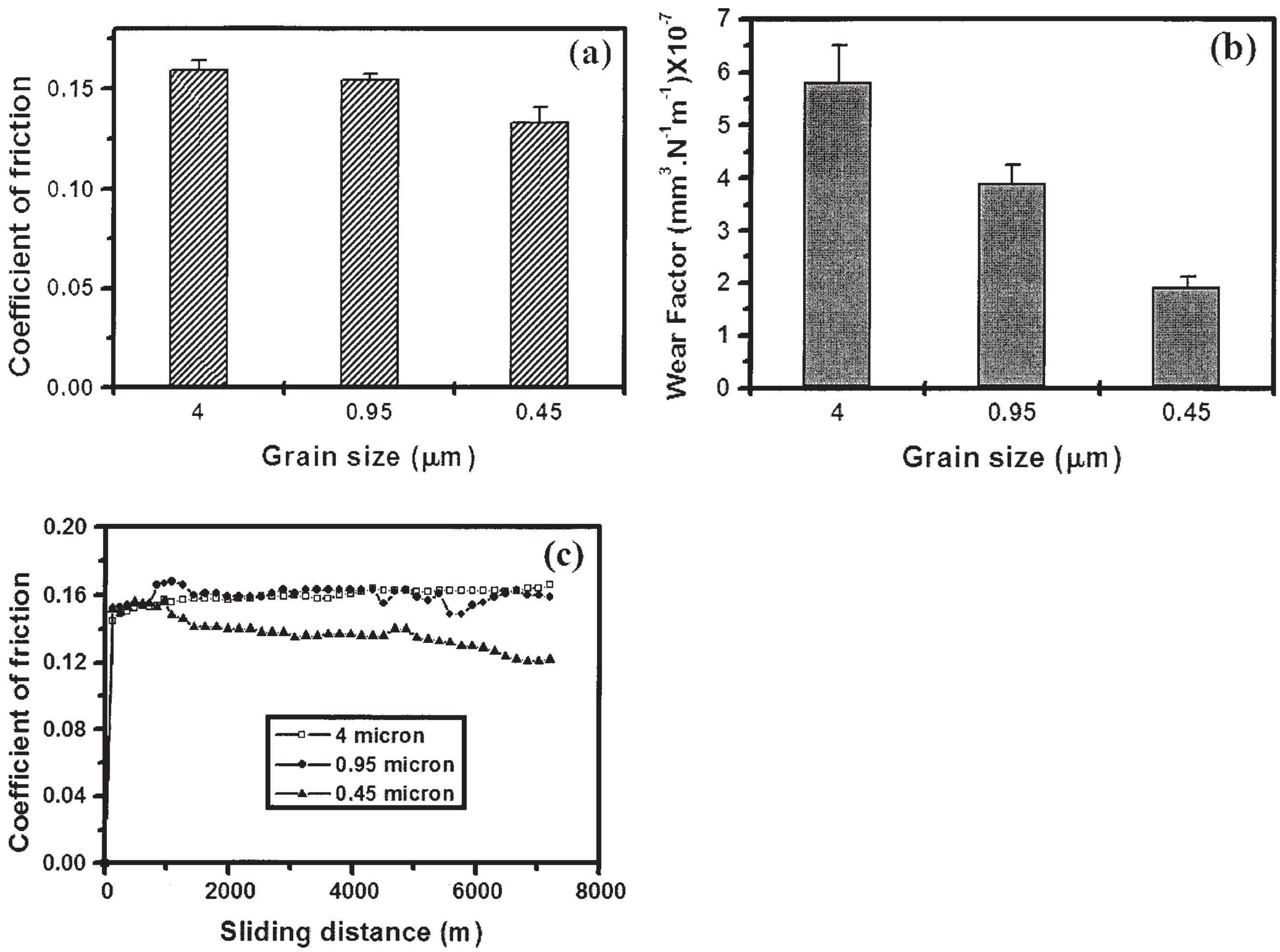

Figure 3. (a) Average coefficient of friction, (b) average wear factor of the alumina used in the present study, (c) variation in coefficient of friction with sliding distance for different alumina in bovine serum. (Test load = 50 N).

smaller grains as observed in the present wear tests can hardly be explained in the light of propagation of bigger cracks. Rather, it can be reasonably attributed to the plausible decrease in grain boundary toughness with increasing grain size which occurs from greater accumulation of internal residual stresses at the boundary of the larger grains. The residual stress arises because of thermal expansion anisotropy of noncubic material (e.g. alumina) during cooling from the sintering temperature.[26,27] For alumina of larger grain sizes, this lower value of grain boundary toughness makes the grain boundaries weak and more vulnerable to crack growth. As a result, under the stresses induced by wear, the propagation of microcracks around a single grain or a cluster of grains and their subsequent coalescence

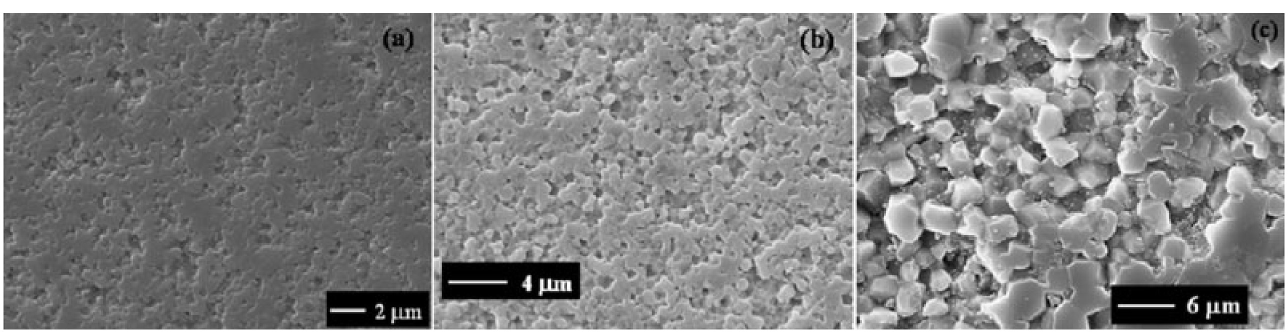

Figure 4. SEM topography of the worn out alumina test samples showing the extent of maximum grain pull out for (a) $G = 0.45$ μm, (b) $G = 0.95$ μm, (c) $G = 4$ μm.

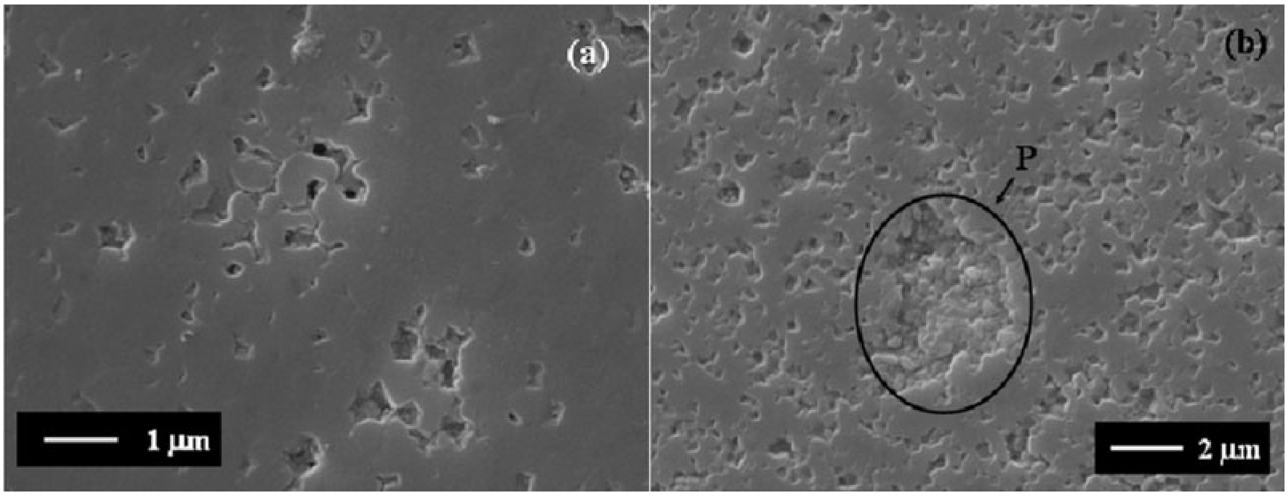

Figure 5. (a) Test samples at 10 N load showing mild grain pull out, (b) worn surface at higher load (i.e. 50 N) showing occasional removal of large segment with a dimension of several grain diameters (zone 'P') for $G = 0.45$ μm.

easily occur in bigger grained alumina. This ultimately leads to pull out of material from the respective area.

Cho et al.[13] have shown that during wear, the accumulation of severe contact stresses at the grain boundary can cause the propagation of the flaws from pre-existing grain boundary triple point defects also. They also suggested the governing equation [Eq. (1)] to determine the wear-induced stress (σ_D) required for grain boundary micro-fracture to cause grain pull-out by propagation of microcracks through the boundary of the grain.[13]

$$\sigma_D = \sigma_I\left[(l/l_*)^{-1/2} - 1\right] \quad (1)$$

where, σ_I = internal tensile stress because of to thermal expansion anisotropy, the maximum value of σ_I can be = 100 MPa,[28] l = grain size of the alumina used in the experiment, l_* = critical grain size limit of alumina for spontaneous microfracture due to thermal expansion anisotropy.[26] For the present set of data, it shows that the σ_D increases abruptly with decreasing grain size (Table II), which in turn points out that the growth of microcracks through the grain boundary of smaller grains becomes increasingly difficult. From Transmission electron microscopy of the worn out alumina samples too, dislocation pile ups at the grain boundaries of larger grained material has been reported to occur at a greater extent than that in case of smaller grains[13] which also supports the proposition of more vulnerable grain boundary in larger grains. Moreover, a single grain pull-out produces a larger defect on the surface for the bigger grained alumina which acts as a more potential source for further grain dislodgement. The mutual combination of all these factors results in superior wear resistance of submicron grained alumina in comparison with coarser grained ones.

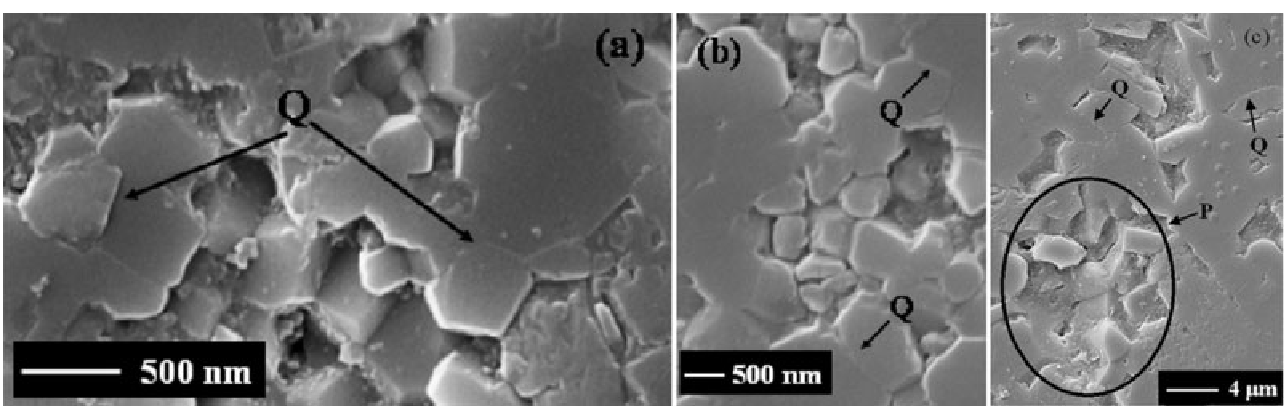

Figure 6. SEM topography of small selected areas of worn out test samples showing evidences of grain boundary microcracking (a) $G = 0.45$ μm, (b) $G = 0.95$ μm, (c) $G = 4$ μm.

TABLE II
Wear-Damage-Induced Stress Required to Cause Grain Boundary Microfracture for Different Grain Sizes of Alumina Used in the Present Study

Grain Size, l (μm)	Wear Damage Stress, σ_D (MPa)
400	0 (Spontaneous Microfracture Limit)
4	900
0.95	1952
0.45	2881

CONCLUSIONS

In bovine serum, wear factor of submicron grained alumina was found to be comparatively lower than that in case of alumina with higher average grain sizes. Grain pull out or localized grain dislodgement caused by coalescence of grain boundary microcracks has been found to be the basic wear mechanism of alumina though in submicron alumina, the extent of cracking and pull-out was substantially less than that of higher grained material. No significant differences in basic wear mechanisms of submicron alumina were found with 10 N and 50 N loads except the fact that the severity of grain pull-out increases with increasing load. The average coefficient of friction of alumina in bovine serum for the selected load range did not significantly vary with grain size.

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