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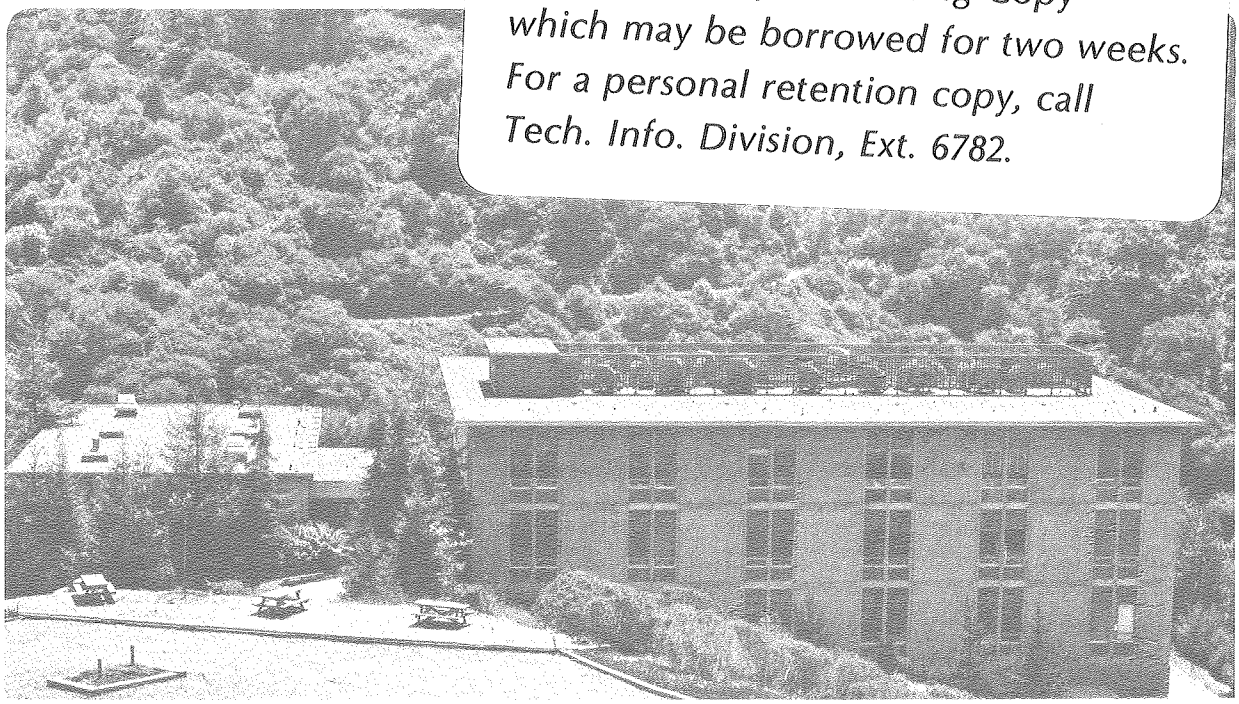

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DISCLAIMER

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1. INTRODUCTION

In a series of previous reports the effect of silica impurity on aggregation state and on electropheretic, pressing, filtering and sintering behavior on alumina powders was presented. The results obtained showed that the silica surface impurity plays an important role in the ceramic processing of powders by (a) decreasing the pH values of the isoelectric point (i.e.p.), which affects the aggregation state of the powder, and (b) decreasing the compactability and the activation energy for the initial stage of sintering.

In this phase of the studies emphasis was given to the effect of the presence of silica impurity on the toughness and fracture behavior of alumina samples.

2. EXPERIMENTAL

Alumina powder (Alcoa A-14) with a particle size range of 2 to 5 μm has been used. X-ray diffraction analysis showed only α-Al_2O_3. It was submitted to the following treatments:

a. 25g were treated with 500 ml. of 0.2N HF for 2 hrs with constant shaking, filtered and washed with triple-distilled water (spectrographic analyses of the untreated and HF-treated powders are given in Table I);

b. Slurries of HF-treated and untreated powders were prepared in polyethylene bottles with a concentration of 25 g/l and a pH of ∿4.5 (hign zeta potential) by adding $HClO_4$, shaking for 48 hrs, filtering and drying the cakes at 60°C for 48 hrs;

c. Disks of 25.4 mm diameter were prepared with untreated and HF-treated powders by hot-pressing in a graphite die under vacuum at a

pressure of 35 MN/m^2 for 1 hr at 1500°C;

d. Fracture toughness was determined on specular polished specimens by an indentation technique with the Vickers indenter using an applied load of 25 Kg;

e. The specimens were thermally etched at 1400°C for 3 hrs and examined by SEM, the average grain size being determined by the intercept method using random straight lines drawn directly on the micrographs[4], and

f. Thinned specimens of untreated and HF-treated samples were prepared for analyis by TEM and STEM in a Philips 400 electron microscope.

2. RESULTS AND DISCUSSION

The indicated HF-treatment caused the removal of ∿95% of the silica and ∿50% of the calcia impurities as seen in Table I. This fact indicates that almost all of these impurities are present on the surface of the alumina powder and exist in an available form because mullite is not subject to this solution.

Moya et al.[2] reported that the silica impurity shifts the i.e.p. of the alumina powder to the acid pH region causing the alumina to behave as a silica-like compound from an electrophoretic point of view. They further showed that in either case the treatment of the powder at a low pH caused a high Z-potential which kept the powder dispersed and retarded the formation of agglomerates[1]. Hence, this was the purpose of the treatment at pH ∿4.5.

SEM micrographs showed a homogeneous microstructure in both kinds of specimens. The grain size, grain boundary groove width and density

measurements were: 3.0, 3.7 μm; 0.1, 0.4 μm; and 96.8, 94.2 % th. for untreated and HF-treated specimens, respectively.

From the measurements of hardness-H, indentation crack length-C and the indentation impression radius-a, the value of Kc was determined by using the calibration curve developed by Evans and Charles.[5] The average values of the stress intensity factor Kc obtained for untreated and HF-treated samples were 3.0 ± 0.5 and 4.8 ± 0.4 MN $m^{-3/2}$, respectively. These values were obtained by first estimating the quantity $\phi(H/\phi E)^{0.4}/H\sqrt{a}$ by using $E \approx 380$ GN m^{-2} and $\phi \approx 3$, (E and ϕ being Young's modulus and the constraint factor, respectively), and knowing the values of a and H from experimental measurements. The dimensionless parameter $Kc\ \phi\ (H/\phi E)^{0.4}/H\sqrt{a}$ was then obtained from the calibration curve[5] by using the experimentally obtained values of c/a. The ratio of the two quantities yielded the magnitude of Kc.

SEM examination of the indentation fractures showed that the cracks propogate mainly along grain boundaries in untreated samples and through the grains in HF-treated samples. TEM/STEM observations showed frequent pockets of second phase at multiple grain boundary junctions in untreated samples. Corresponding microdiffractions of these pockets confirmed them to be amorphous. Energy dispersive x-ray analysis in the STEM mode revealed the presence of silica in such amorphous pockets while no silica was detected in the center of the alumina grains. The presence of this phase increases the densification rate and exerts a moderate inhibitory effect on the grain growth, as was observed in conventional sintering experiments by Moya et al.[3]

The microstructure of specimens made with HF-treated alumina had a noticeable increase in porosity. TEM observations indicated no amorphous phase at triple points or along any grain boundaries. Also, a dislocation structure was observed along the grain boundaries which was absent in the untreated alumina. This structure, due to the absence of an amorphous phase, indicates the possible existence of anisotropy of the grain boundary energy which introduces a driving force for grain boundary motion. This condition leads to the larger grain size exhibited by the treated alumina.

Much work on polycrystalline alumina has been concerned with the influence of grain size on fracture mechanics parameters[6,7], but only minor attention has been paid to the effect of impurities.

The most accepted value for Kc in polycrystalline aluminas[7,8] is close to 5 MN $m^{-3/2}$. This datum is in agreement with the toughness value determined for the HF-treated samples, which can be considered as pure alumina (Table I).

The decrease of ∿40% in the Kc value in the untreated sample, which has an average grain size very similar to the treated samples, must be due to the presence of the small amount of observed intergranular glassy phase caused by a small amount of silica. This glass flux increases the grain boundary energy and the densification rate, and it is responsible for the intergranular fracture behavior of this material.

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REFERENCES

1. J. A. Pask, Bull. Am. Ceram. Soc., 58:1163 (1979).
2. J. S. Moya, J. Rubio and J. A. Pask, Bull. Am. Ceram. Soc., in press.
3. J. S. Moya and J. A. Pask. To be published in the Proc. of the 9th International Symposium on the Reactivity of Solids, Cracow, Poland, 1980.
4. P. L. Fulman, Trans. AIME, 197:447 (1953).
5. A. G. Evans and E. A. Charles, J. Am. Ceram. Soc., 59:371 (1976).
6. N. Claussen, R. Pabst and C. P. Lahmann, Proc. Brit. Ceram. Soc., 24:139 (1975).
7. B. J. Dalgleish, P. L. Pratt and J. Sandford, Science of Ceramics, Vol. 8:225 (1976).
8. N. Claussen, J. Am. Ceram. Soc., 59:49 (1976).

Table I

Spectrographic Analysis Data of Alumina Specimens

Constituents*	Untreated (%)	HF-treated (%)
Al	Principle constituent in each sample	
Si	0.15	0.01
Ca	0.01	0.005
Fe	0.04	0.03
Mg	0.005	0.003
Ga	0.008	0.007
Ti	0.003	0.002
Ba	0.001	-
Cu	0.001	0.001

*Constituents reported as oxides of the elements indicated. Analysis performed by American Spectrographic Laboratories, Inc., San Francisco, California.