Processing-Related Fracture Origins: III, Differential Sintering of ZrO_2 Agglomerates in Al_2O_3/ZrO_2 Composite

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Large, hard ZrO_2 agglomerates remained in an Al_2O_3/ZrO_2 composite suspension after inefficient ball-milling. The ZrO_2 agglomerates shrank away from the consolidated Al_2O_3/ZrO_2 powder matrix during sintering, producing cracklike voids which were responsible for strength degradation.

I. Introduction

IT WAS previously demonstrated that dry powder routes to powder consolidation can produce large agglomerates which result in large cracklike voids due to differential sintering.[1] In dry powder routes, soft agglomerates are apparently formed either by the spontaneous attraction of particles due to van der Waals forces or by particle cohesion due to surface-tension effects produced by absorbed, atmospheric water. It was also demonstrated that the colloidal/filtration route (commonly known as slip casting) to powder consolidation has great potential for minimizing agglomerate size and therefore the size of the strength-degrading, cracklike voids formed by differential sintering.[2] The objective of this route is to break down all agglomerates and to keep the particles well dispersed in a liquid (using the principles of either electrostatic repulsion or steric hindrance) up to the last moment, when most of the liquid is removed by filtration. This paper points out that theory is sometimes difficult to achieve in practice and catalogs another type of agglomerate which produces strength-degrading, cracklike voids and shows how it is related to powder processing.

II. Experimental Procedure

The initial intention of this work was to reproduce the procedure to make a high-strength Al_2O_3/ZrO_2 material by the colloidal/filtration route described earlier,[2] but to avoid the silicate phase that produces the strength-limiting flaws observed at the fracture origins. In the original work,[2] the silicate phase was traced to the debased-Al_2O_3 mill jar and milling media. Thus, the only change was to use a high-purity Al_2O_3 mill jar and milling media purchased[*] for this task. As reported earlier,[2] the ZrO_2 powder[†] is comprised of submicrometer-sized particles. Most of these particles are in the form of hard agglomerates which can be broken down by attrition only. The Al_2O_3[‡] powder is relatively free of hard agglomerates. As before,[2] the two powders (Al_2O_3/30 vol% ZrO_2) were combined with deionized water at pH 2.5 to produce a suspension containing 25 vol% solids, milled for 18 h, readjusted to pH 2.5, filtered, dried, sintered at 1600°C/2 h, and cut into specimens for flexural strength determinations (inner span: 1.27 cm; outer span: 2.54 cm).

III. Results and Discussion

Strength values were significantly lower than those previously reported (896 MPa),[2] with values ranging between 510 and 572 MPa and an average of 540 MPa.

Fracture origins were examined by SEM to determine if the strength-degrading flaws could be easily traced to some processing step. In all cases, a large, polycrystalline ZrO_2 inclusion contained within a similarly shaped, but somewhat larger hole, was observed at the fracture origin, as shown by the typical example in Fig. 1(*A*). A matching hole was observed at the fracture origin on

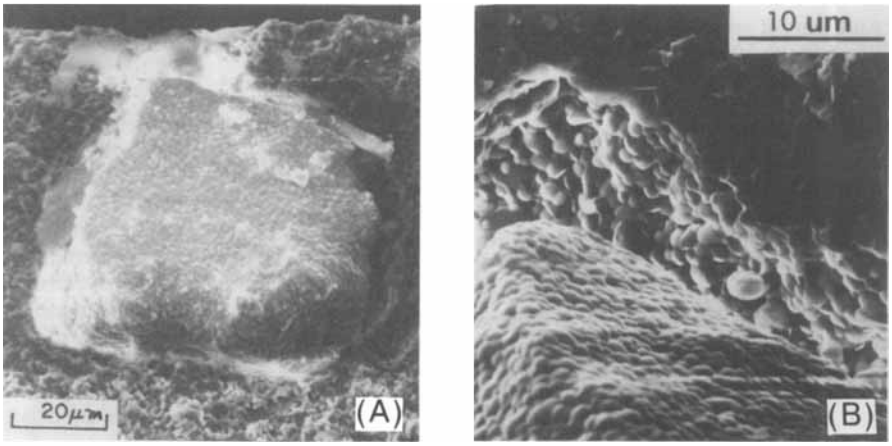

Fig. 1. (*A*) ZrO_2 polycrystalline inclusion at fracture origin. (*B*) Micrograph showing that ZrO_2 inclusion surface and Al_2O_3/ZrO_2 surface from which ZrO_2 agglomerate had separated are internal sintered surfaces.

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[*] 99.5% alumina grinding media, Coors Porcelain Co., Golden, CO.

[†] Zircar Products Inc., Florida, NY.

[‡] Alcoa A-16SG, Aluminum Company of America, Pittsburgh, PA.

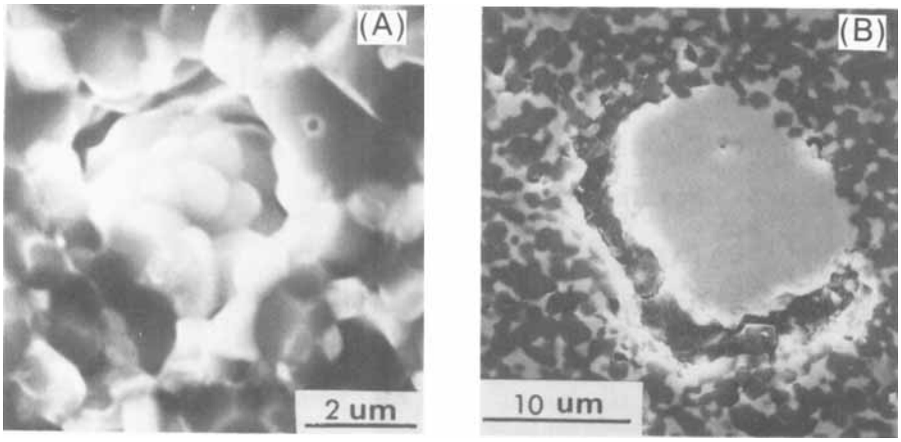

Fig. 2. (*A*) ZrO_2 inclusion resulting from differential sintering intercepted by crack. (*B*) Cracklike void produced by differential sintering of ZrO_2 agglomerate.

the other half of the fractured specimen, which could have been mistaken as a void if the other half was not examined. The topography of the surfaces within the hole and those bounding the ZrO_2 inclusion were typical of internal, sintered surfaces (Fig. 1(*B*)) and was distinct from that of the surrounding fracture surfaces. Smaller ZrO_2 inclusions, which were separated from the composite Al_2O_3/ZrO_2 matrix with a crack-shaped void, were also observed on the fracture surfaces but remote from the fracture origin, as shown in Fig. 2(*A*). Such cracklike voids were too small to be the strength-degrading flaw relative to the much larger ones at the fracture origin. These smaller ones (Fig. 2(*A*)) were simply intercepted by the propagating crack. Polished surfaces also revealed the polycrystalline ZrO_2 inclusions partially surrounded by their cracklike void, as shown in Fig. 2(*B*). Measurements of the matrix-agglomerate separations suggest that the bulk density of the ZrO_2 hard agglomerates was $\approx$40% of theoretical prior to sintering.

It is obvious that not all of the hard ZrO_2 agglomerates were broken down during milling. The examples chosen here resulted from an inefficient milling operation, i.e. less than optimum powder charge. Although it is an extreme example, work has shown that, although proper milling does reduce the size of most hard agglomerates, it does not eliminate all, nor does it guarantee that all hard agglomerates are less than a given size. Besides, milling introduces contaminants—even the high-purity Al_2O_3 will introduce its wear product, viz. 10 to 20 μm fractured Al_2O_3 grains.

Our current work shows that hard agglomerates greater than a given size (e.g. >1 μm) can be eliminated by sedimentation (a processing step that could be automated with continuous centrifuging).

References

[1] F. F. Lange, "Processing Related Fracture Origins: I, Observations in Sintered and Isostatically Hot-Pressed Al_2O_3/ZrO_2 Composites"; this issue, pp. 396–98.

[2] I. A. Aksay, B. I. Davis, and F. F. Lange, "Development of Uniformity in Al_2O_3/ZrO_2 Composites by Colloidal/Filtration Route"; unpublished work.

[3] F. F. Lange and M. Metcalf, "Processing Related Fracture Origins: II, Agglomerate Motion and Cracklike Internal Surfaces Caused by Differential Sintering"; this issue, pp. 398–406.

Effect of Silver Doping on the Physical and Electrical Properties of PLZT Ceramics

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Additions of small amounts of silver to a PLZT dielectric with emphasis on the 88/12/70/30, Pb/La/Zr/Ti, composition were investigated. It was found that a few mole percent of Ag^{1+} could be incorporated into the PLZT lattice as a large acceptor cation and that it tended to reduce the lead vacancies, which are normally generated by the substitution of La^{3+} in the PLZT dielectric. The addition, up to 2 mol% of silver, decreased the 25°C dielectric constant from 2300 to 1700. However, the temperature coefficient of capacitance was improved to ±15% between −55° and +125°C, and the dissipation factor was reduced from 1.5 to 0.5%. Although the gravimetrically measured lead loss appeared to depend on the relative vapor pressure of lead oxide during sintering, the compensation mechanism of Ag^{1+} was not affected.

I. Introduction

The system lanthanum-modified lead zirconate titanate has been extensively studied[1,2] for electrooptic application. In the antiferroelectric region this dielectric offers exceptionally good electrical properties, i.e. relatively high dielectric constant (*K*), low dissipation factor (DF), and low sensitivity to dc bias, as has been pointed out by Biggers and others.[3–6] For an X7R capacitor application,* however, this type of dielectric suffers from a significant loss in permittivity at low temperature (less than −30°C).

We have discovered[7–10] that addition of small amounts of silver tends to broaden the temperature coefficient of capacitance (TCC), decrease the dissipation factor (DF), and further improve the voltage coefficient, but at some loss in the dielectric constant (*K*).

Accordingly, the objective of this study was to investigate the effect of silver doping on the chemistry of this PLZT system (i.e. vacancy compensation) and its subsequent effect on the physical and electrical properties.

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