

Transformation toughening of β'' -alumina by incorporation of zirconia

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It is shown that zirconia is chemically compatible with lithia-stabilized β'' -alumina and that incorporation of tetragonal zirconia in the matrix of β'' -alumina leads to an improvement in fracture toughness and four-point bend strength without significantly affecting ionic conductivity. Chemical compatibility is demonstrated by reacting α -alumina with sodium zirconate at 1250° C which leads to the formation of β'' -alumina and free zirconia. The fracture toughness as measured using the indentation technique is found to increase with increasing crack length.

1. Introduction

It was first reported by Garvie [1] that partially stabilized zirconia containing finely dispersed metastable tetragonal zirconia in a matrix of cubic zirconia has significantly superior mechanical properties compared to fully stabilized cubic zirconia. Subsequently, several researchers [2–8] have shown that the strength and fracture toughness of ceramic bodies containing finely dispersed tetragonal zirconia are considerably higher when compared to the same ceramics without tetragonal zirconia. The origin of the toughening effect lies in the fact that the tetragonal zirconia particles convert to the monoclinic polymorph in the near stress field of a propagating crack. The strength of ceramic bodies containing tetragonal zirconia can also be improved substantially by surface grinding. The process of grinding converts the tetragonal zirconia particles in the near surface region to the monoclinic polymorph. This leads to the development of compressive stress on the surface due to the lower density of the monoclinic zirconia, which in effect increases fracture strength. While most of the work has been on partially stabilized zirconia, Claussen [9] has shown that the mechanical properties of alumina can also be improved by incorporating fine particles of zirconia, which are retained metastably in the tetragonal form at room temperature. The magnitude of this toughening effect, which depends upon: 1. the volume

fraction of tetragonal zirconia, 2. the size of the zirconia particles and 3. the elastic properties of the matrix, also depends upon temperature. Below $\sim 500^\circ\text{C}$, the improvement in toughness is significant but at elevated temperatures it is rather marginal. Thus, for high-temperature structural applications it is doubtful that transformation toughening would be important. However, there are likely to be several low temperature applications for ceramics of technological importance whose performance could be significantly improved by transformation toughening. It is the object of the present paper to report such an application.

Sodium β'' -alumina is currently being used as a solid electrolyte for application in the sodium–sulphur battery and the sodium heat engine [10, 11]. The sodium–sulphur battery operates at a temperature of about 350° C. It has long been known that under certain conditions, the β'' -alumina solid electrolyte undergoes strength degradation. This degradation manifests itself in the form of cracks filled with liquid sodium. It has also been suggested that electronic conductivity may play a significant role in the onset of propagation of degradation. The sodium-filled cracks propagate through the thickness of the solid electrolyte leading to the failure of the battery. The degradation of the solid electrolyte has been modelled by several researchers [12–17]; common

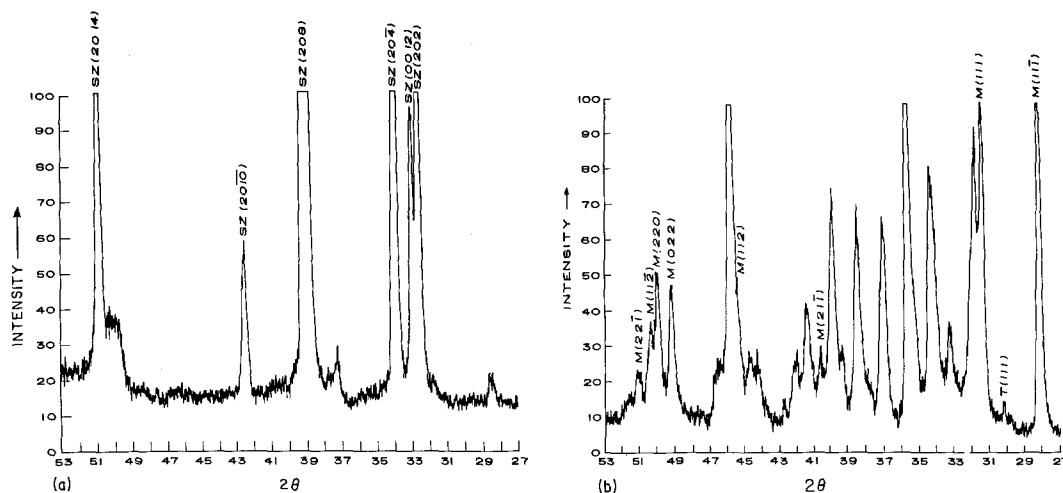


Figure 1 X-ray diffraction pattern of (a) Na_2ZrO_3 taken with $\text{CuK}\alpha$ and (b) a powder mixture of Na_2ZrO_3 and Al_2O_3 which was calcined at 1250°C for 5 h. Note that no Al_2O_3 and Na_2ZrO_3 can be seen. The reaction products are β -alumina and zirconia.

to most of them is the concept of sodium under pressure in cracks. These models show that degradation of the solid electrolyte will occur above a certain current density, termed the critical current density, i_{cr} , during the charging mode of the battery. Based on the Poiseuille pressure model, it has been shown that the current density above which degradation occurs is proportional to the fourth power of K_{Ic} (the fracture toughness) [17]. Thus, modest improvement in K_{Ic} should lead to a significant improvement in i_{cr} . Specifically, if K_{Ic} is doubled, the critical current density would increase sixteen times, all other factors remaining the same. Should this be the case, the doubling of K_{Ic} would have significant economic advantages with regard to the sodium-sulphur battery. For example, not only would the battery life be enhanced, but the charging time could be drastically reduced by increasing the charging current density. Reduced charging time is expected to be an important factor in the viability of the electric vehicle as an attractive alternative to petrol-powered vehicles.

One possible method of increasing K_{Ic} of β'' -alumina is by incorporation of tetragonal zirconia as a finely dispersed second phase. It is essential that β'' -alumina and zirconia do not react with each other and do not have significant solubility for each other, otherwise the fundamental and necessary ionic properties of β'' -

alumina could be affected deleteriously. It is the object of the present paper to report our findings on the transformation toughening of β'' -alumina.

2. Experimental procedure and results

2.1. Chemical compatibility of ZrO_2 with β'' -alumina

For the transformation toughening of any material using zirconia as a dispersed phase to be possible, the premier requirement is the chemical compatibility of zirconia with the material in question i.e. zirconia should not react with or go into solution in the material when fired at elevated temperatures for sintering but must remain as a separate phase. Since sodium zirconate (Na_2ZrO_3) is known to be a stable compound, it is essential* to determine if it is stable in the presence of α -alumina. Specifically Na_2ZrO_3 should react with Al_2O_3 to form β -alumina or β'' -alumina or some other Na-aluminate and release ZrO_2 .

Na_2ZrO_3 powder was prepared by calcining a mixture of Na_2CO_3 and ZrO_2 in equimolar proportion at 1250°C for 2 h. The resulting powder was single phase Na_2ZrO_3 as evidenced by the X-ray diffraction pattern shown in Fig. 1a. Subsequently, Na_2ZrO_3 and Al_2O_3 were mixed in a 1 to 6 ratio (molar) and calcined at 1250°C for 5 h. X-ray diffraction revealed that no Na_2ZrO_3 or Al_2O_3 were then present as shown in Fig. 1b. The X-ray diffraction pattern indicated the presence

*To the author's knowledge the standard free energy of formation of β'' -alumina as a function of temperature is not known.

of tetragonal and monoclinic ZrO_2 along with β'' -alumina. To demonstrate the chemical compatibility between lithia-stabilized β'' -alumina and ZrO_2 , a mixture of β'' -alumina and ZrO_2 was calcined at $1250^\circ C$ for 2 h. The X-ray diffraction pattern indicated the presence of β'' -alumina and monoclinic and tetragonal zirconia. These experiments therefore show that β'' -alumina and zirconia are chemically compatible.

2.2. Fabrication of $ZrO_2 + \beta''$ -alumina specimens

β'' -alumina powder of nominal composition 8.85 wt% Na_2O –0.75 wt% Li_2O and 90.4 wt% Al_2O_3 was prepared* using zeta lithium aluminate ($Li_2O:5Al_2O_3$) and the source of lithium [18]. Unstabilized zirconia† of particulate size in the range of a few hundred angstrom units (agglomerate size in the range of a few tenths of a micron) were mixed with β'' -alumina powder in weight per cents ranging from 1.5 to 25 wt% ZrO_2 . The mixture was wet milled in acetone for up to two days. The powder was subsequently dry milled for 24 h. Rectangular bars were die-pressed, isostatically pressed and sintered at $\sim 1600^\circ C$ in sealed platinum capsules.

Samples containing 1.5 and 3.0 wt% ZrO_2 were sintered at $1600^\circ C$ for various lengths of time ranging from 3 min to 2.5 h. Samples sintered for 1 h or longer were coarse grained while the samples sintered for less than 15 min were extremely fine grained with a corresponding density of about 98% of the theoretical. No significant improvement in strength was observed. Ground samples containing 15 wt% ZrO_2 were about 97% dense and exhibited four-point bend strengths‡ ranging from 2.275×10^5 to 3.103×10^5 kNm^{-2} (33 to 45 ksi). The strength of zirconia-free β'' -alumina samples similarly sintered (~ 5 min at $1600^\circ C$) was between 1.517×10^5 and 1.724×10^5 kNm^{-2} (22 and 25 ksi) even though their density was in excess of 98% of the theoretical. The ionic resistivities§ of both β'' -aluminas (with and without zirconia and sintered at $1600^\circ C$ for 5 min) was $6.4 \Omega cm$ at $300^\circ C$. A few of the samples with zirconia did have resistivities as high as $22 \Omega cm$ at $300^\circ C$ although for most samples it was below $7 \Omega cm$.

*Ceramatec Inc., Salt Lake City, Utah.

†Zircar Inc.

‡Unground samples exhibit similar high strength.

§ $NaNO_3$ – $NaNO_2$ eutectic was used as the electrode material. The measurement was carried out at 50 kHz which yields the d.c. resistance of the specimen.

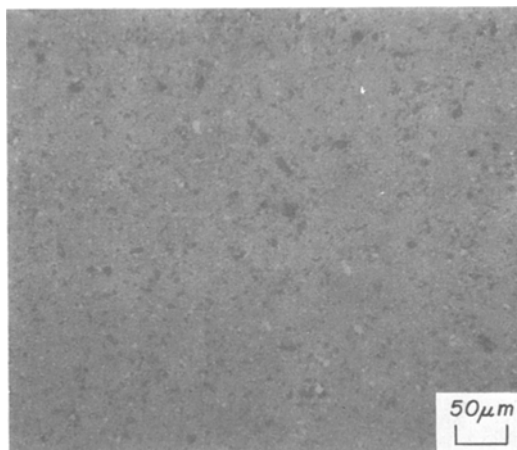


Figure 2 A photomicrograph of β'' -alumina + ZrO_2 . (The sample was sintered at $1600^\circ C$ for 5 min.)

The samples sintered for longer times (1 to 2.5 h) contained only monoclinic zirconia and did not exhibit any improvement in strength.

Samples containing 25 wt% ZrO_2 had strengths as high as 3.792×10^5 kNm^{-2} (55 ksi) even though their density was about 97% of theoretical. These specimens exhibited very high ionic resistivities. Presumably, the distribution of zirconia must be along the grain boundaries as a continuous phase. X-ray diffraction of all the samples with zirconia revealed the presence of β'' -alumina and predominantly tetragonal zirconia with small amounts of monoclinic zirconia.

The as-sintered samples contained zirconia in the predominantly tetragonal form despite a significant fraction of zirconia above a particle size of 2 to $3 \mu m$ as viewed under the optical microscope. Fig. 2 shows a typical optical micrograph of a sample containing 15 wt% zirconia. Samples when examined by X-ray diffraction after grinding showed that a large amount of metastably retained zirconia was converted to the monoclinic polymorph. Typical X-ray diffraction patterns before and after grinding are shown in Fig. 3a and 3b, respectively. The process of grinding which promotes the tetragonal \rightarrow monoclinic transformation would be expected to develop compressive surface stresses thereby leading to an increase in strength. Also, the presence of compressive stresses

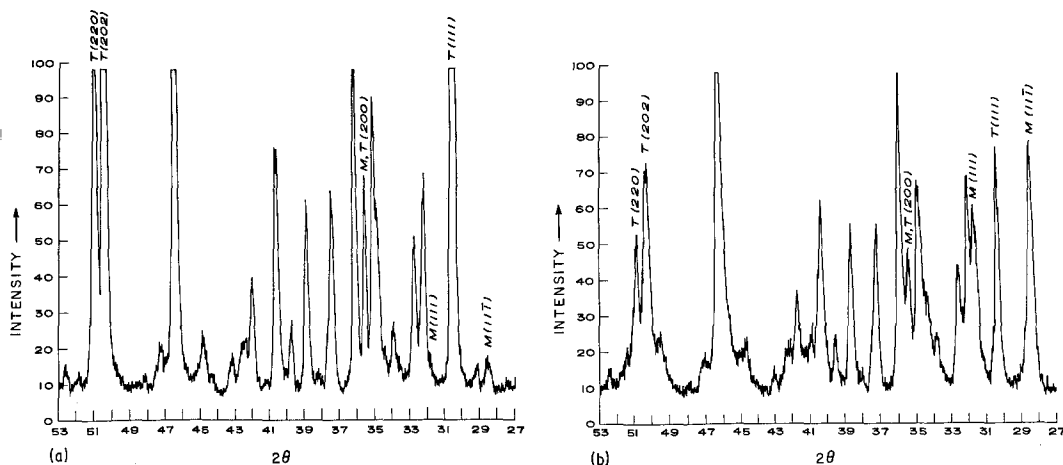


Figure 3 X-ray diffraction pattern of (a) a sintered sample of β'' -alumina with 15 wt% zirconia (note that zirconia is predominantly of the tetragonal form) and (b) the sample shown in Fig. 3a after the surface was ground. As seen in the figure, a significant amount of tetragonal zirconia converted to the monoclinic polymorph upon grinding.

should tend to retard electrolytic degradation processes.

2.3. Fracture toughness

A sample containing 15 wt% zirconia was polished down to a $1\ \mu\text{m}$ finish. Vickers hardness indentations were introduced at loads ranging from 14 to 90 N and the length of radial cracks was measured. The apparent fracture toughness, K_{Ic}^a , was evaluated using the method of Evans and Charles [19]. Fracture toughness ranged from 5.0 to $8.0\ \text{MN m}^{-3/2}$; higher values of K_{Ic}^a corresponded to higher values of the indentation load. Fracture toughness of zirconia-free β'' -alumina on the other hand was between 2.5 and $3.0\ \text{MN m}^{-3/2}$. Thus, addition of zirconia leads to a significant enhancement of K_{Ic}^a . A plot of K_{Ic}^a against $C^{1/2}$, where C is the crack length, is shown in Fig. 4.

3. Discussion

The objective of the present work was to demonstrate that zirconia and β'' -alumina are mutually chemically compatible and that β'' -alumina can be transformation-toughened by incorporating finely dispersed zirconia in its tetragonal polymorph. Considerable developmental work would be required to maximize strength and density without altering the ionic properties significantly. In the as-sintered condition, the majority of the zirconia was in the tetragonal form despite the fact that a significant fraction of the zirconia was of particle size in excess of $1\ \mu\text{m}$. When the specimens are ground, zirconia particles convert martensitically to the monoclinic phase. This should lead to a

development of compressive stress on the surface. The K_{Ic}^a as determined by the indentation technique [19], was found to be crack-length dependent. Specifically, K_{Ic}^a increases with increasing crack length as shown in Fig. 4. The increase in K_{Ic}^a with increasing crack size, C , may be attributed to the existence of compressive stress on the surface due to grinding. If this is so, the slope of apparent

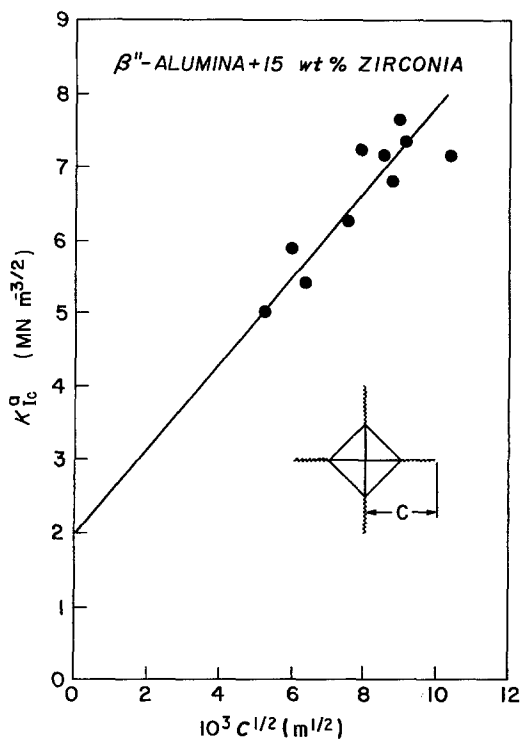


Figure 4 A plot of K_{Ic}^a against $C^{1/2}$. Indentations were introduced on a ground and polished surface.

K_{Ic}^a against $C^{1/2}$ should be linearly proportional to the magnitude of the stress. $K_{Ic}^a = K_{Ic}$ (intrinsic) $- \sigma AC^{1/2}$, where σ = residual stress (negative for compression) and A = constant, dependent on crack geometry. I_{Ic} (intrinsic) = K_{Ic} for zirconia-free β'' -alumina.

Assuming a through crack ($A = \pi^{1/2}$) the magnitude of the compressive stress ($|\sigma|$) corresponds to 325 MN m^{-2} . The sample contained 15 wt% ZrO_2 , i.e. 8 vol% ZrO_2 . The tetragonal to monoclinic volume expansion is about 7%. Therefore, the volume strain = 5.6×10^{-3} and the linear strain = 1.87×10^{-3} . Based on a Young's modulus (E) for β'' -alumina of $2.07 \times 10^{11} \text{ N m}^{-2}$, the calculated value of stress ($\sigma = \epsilon E$) is about 387 MN m^{-2} . In view of uncertainties regarding crack geometry and the exact volume change on transformation and the fact that not all the tetragonal phase transforms as assumed in the calculation, the agreement between experimental and the calculated values of the surface stress appears reasonable.

While improved strength and fracture toughness have resulted from the incorporation of zirconia in β'' -alumina, it remains to be seen whether this improvement in mechanical properties leads to an increase in the actual cell life in the case of the sodium-sulphur battery. It is essential that the addition of zirconia should not lead to an increase in electronic conductivity. Furthermore, for zirconia toughening to be beneficial in the sodium-sulphur battery, it is essential that the addition of zirconia should not lead to increased charge transfer resistance or poor wetting as this could accelerate degradation processes.

Other things remaining constant, if K_{Ic}^a can be improved substantially, the critical current density [17] above which degradation occurs can be raised by more than an order of magnitude. An increase in critical current density could mean longer cell life and shorter charging time, both of which are vital to the economic feasibility of the sodium-sulphur battery.

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