

Stabilization of tetragonal phase in polycrystalline zirconia

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It is shown that the tetragonal phase can be stabilized in the sintered body of a partially stabilized zirconia (PSZ) containing low concentrations of yttria. Such sintered body containing the metastable phase undergoes stress-induced phase transformation by the absorption of thermal or mechanical stress and exhibits strengths in excess of 690 MPa (100 ksi).

1. Introduction

Zirconium dioxide, ZrO_2 (zirconia), undergoes a displacive (martensitic) transformation on cooling at temperatures between 1200 and 1000° C. This temperature corresponds to a change from a high-temperature tetragonal to a low-temperature monoclinic structure. The structure change is associated with a volume increase (~9%) on cooling. ZrO_2 has also a cubic structure at extremely high temperature (~2370° C).

The fundamental concept in the engineering use of zirconia is to “alloy” the pure ZrO_2 with enough of another oxide to fully or partially stabilize the cubic structured phase. However, the stabilization of the tetragonal phase* (at temperatures below the equilibrium transformation temperature) has always been an interesting proposition in this alloy system because of its martensitic transition to monoclinic phase. In this respect, ZrO_2 alloy system offers a unique opportunity for studying one of the most important reactions which have been so basic to the structure and property control in the metallic system.

In recent years, [1–4] powders of ZrO_2 containing tetragonal phase at room temperature were prepared. More recently, [5, 6] the existence of tetragonal zirconia in sintered bodies of partially stabilized zirconia (PSZ) has also been reported. The stabilizing oxides were yttria [5] and calcia [6]. This paper describes the details of phase studies in PSZ containing yttria.

2. Experimental procedure

The experiments were conducted with partially stabilized zirconia (PSZ) containing a low percentage of yttria. The particle size of the powder was small ranging from 100 to 300 Å (Fig. 1). X-ray examination of the powder indicated that both tetragonal and monoclinic phases were present.

The powder was pressed into discs and bars and sintered to dense bodies. A standard Norelco X-ray diffractometer, with Ni-filtered $CuK\alpha$ radiation, was used to determine the phases present. Line traces were obtained over a wide range of 2θ values, but the emphasis was placed on that part of the profile where $2\theta = 25^\circ - 35^\circ$, as this contained the two strongest lines of the monoclinic phase at $\sim 28.3^\circ$ (111) and $\sim 31.7^\circ$ (111) and the

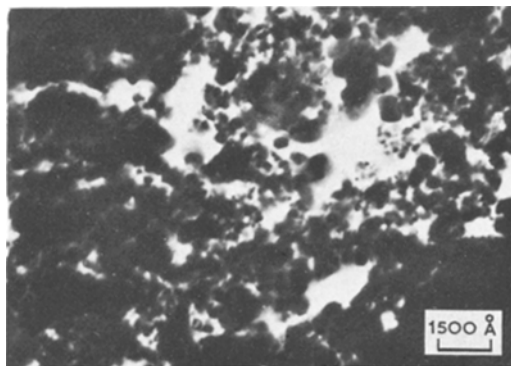


Figure 1 Electron micrograph of PSZ powder (bright field imaging mode).

*The possibility of stabilizing the tetragonal phase at room temperature was first presented on November 2, 1973, and later proposed in a joint proposal with Pennsylvania State University to NSF in April, 1974.

strongest line of the metastable tetragonal phase at $\sim 30.5^\circ$ (111). The percentage of phases was calculated from the relative intensities of the two monoclinic peaks (11 $\bar{1}$) and (111) and the tetragonal peak (111) after correcting for the background counts. Similar approach was taken by Mitsuhashi *et al.* [4], for powder ZrO₂ containing tetragonal phase.

X-ray diffractometer traces were obtained on the as-received powder, heat-treated powder, sintered discs, as well as on discs which were broken and ground to powder.

3. Results and discussion

3.1. Stabilization of tetragonal phase in ZrO₂

Sintering studies indicated that the dense bodies can be routinely obtained at relatively low temperatures ($<1500^\circ\text{C}$) and the content of tetragonal phase in the polycrystalline ZrO₂ ranged from 98 to 10%, depending on the sintering conditions. Fig. 2 illustrates the typical diffraction line traces of a nearly 100% tetragonal ZrO₂ specimen. The traces were made over a range of 2θ values (29° to 76°) so that tetragonal peaks at various reflections can be clearly indexed. It should be noted that (111) peak is the strongest. Should a cubic phase be present in the specimen, peaks would appear in places marked by the arrows. The inspection of the peaks indicate that there is a hint of the presence of a minor cubic phase associated with the tetragonal phase. Because of overlap of peaks, however, this uncertainty could not be resolved. Since the amount of cubic phase, if at all present, would be very small, we have ignored its presence in the interpretation of the data.

The line traces shown in Fig. 2 are in agreement with the traces reported in the literature for both the powder [4] and the solid [6] ZrO₂ containing tetragonal phase. The estimate of lattice parameters are also in good agreement with the literature values. Scott [7] has reported $a = 5.091$ to 5.125 Å and $c = 5.150$ to 5.185 Å for yttria stabilized zirconia, containing several mol% of YO_{1.5}. Garvie *et al.* has reported tetragonal peaks at (400) reflections which yields $a = 5.10$ Å and $c = 5.19$ Å. For the same peaks (illustrated in Fig. 2) we calculate $a = 5.10$ Å and $c = 5.184$ Å. Using these values of a and c , the d -spacings of all the reflections shown in Fig. 2 were calculated and compared with measured " d " spacings from the line trace. The measured and calculated values agree well as shown in Table I. The d -spacings obtained for 111 reflection can be further compared with $d = 2.947$ to 2.952 Å, obtained by Mitsuhashi *et al.* [4] for powders containing 80 to 100% tetragonal phase.

A final point to note is that there is no (400)

TABLE I Comparison of the measured and calculated " d " spacing for tetragonal ZrO₂

Plane	d (Å) (Measured)	d (Å) (Calculated)
111	2.964	2.960
002	2.596	2.592
200	2.553	2.550
202	1.819	1.818
220	1.804	1.803
113	1.560	1.556
311	1.541	1.540
222	1.481	1.480
004	1.296	1.296
400	1.275	1.275

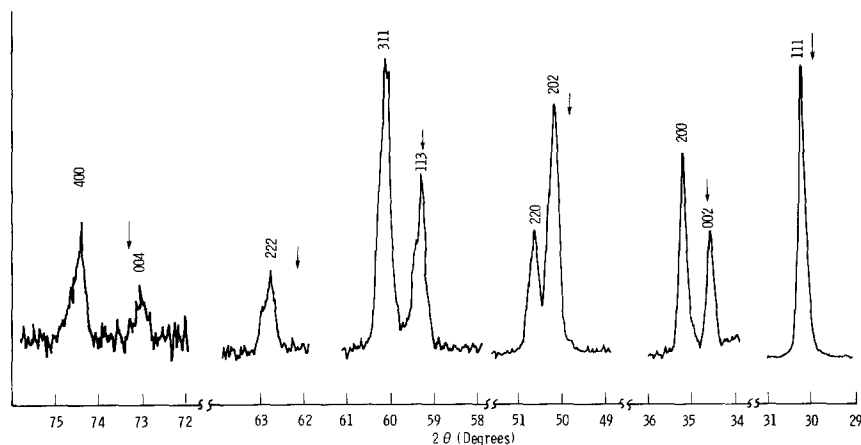


Figure 2 X-ray diffraction pattern of tetragonal ZrO₂.

cubic peak in the specimen, which was reported by Garvie *et al.* [6] for their PSZ, leading to the belief that the present material is different from what they have reported.

3.2. Stress-induced phase transformation

The tetragonal-monoclinic transformation in ZrO_2 is known to be martensitic. The clear demonstration that the metastable tetragonal phase can be retained at temperatures well below the equilibrium transformation temperature has important consequences. For one thing, like metastable austenitic steel, it undergoes a stress-induced phase transformation. Both thermal and mechanical treatments were found to induce phase transformation in ZrO_2 containing tetragonal phase.

When heated above a certain critical temperature, specimens containing high tetragonal phase suddenly changed to monoclinic phase on cooling, often accompanied by cracking of the specimens. This was also reflected in the sintering characteristics of the powder. As shown in Fig. 3, nearly ~100% tetragonal phase was obtained by sintering ZrO_2 to 1400 to 1450°C; as the sintering temperature was raised to 1500°C and beyond*, there was a sudden decrease in the tetragonal phase on cooling and a corresponding increase in the monoclinic phase. This behaviour is believed to be due to a change in grain size. Whereas a grain size of <0.3 μm was observed in PSZ containing a high amount of tetragonal phase, a larger grain size was observed with high monoclinic phase. Grain growth appears to trigger transformation or provide active nucleation site [4] for phase transformation.

The powder behaved somewhat differently under conditions of thermal treatment. In contrast to a discontinuous decrease in tetragonal phase as was observed with sintered disc, the powder showed a continuous decrease in tetragonal phase (with corresponding increase in monoclinic phase) with increasing temperature and time. As shown in Fig. 4, the higher the temperature and longer the time, the greater the conversion on cooling.

The difference in behaviour between the compact disc and the powder is believed to be due to the difference in the behaviour of constrained grains in the disc compared to the free particles in the powder. The free particles have larger surface area compared to that of the grain located inside

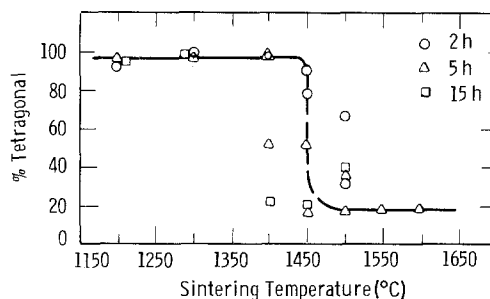


Figure 3 Influence of sintering temperature and time on the formation of tetragonal phase in PSZ ceramics.

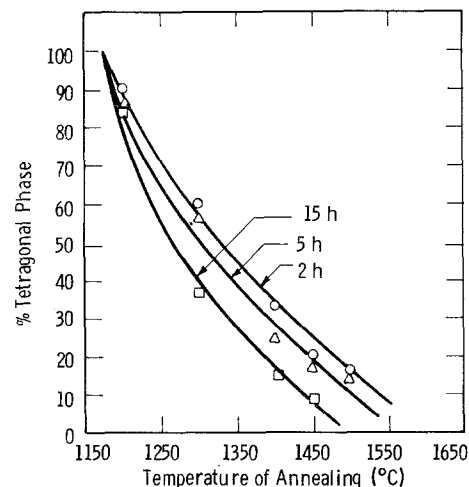


Figure 4 Influence of annealing temperature and time on the phase transformation of PSZ powder.

the disc, or even at the outer surface of the disc. Inspection of Fig. 4 further indicates that the phase transformation in the powder is a kinetic process having a dependence on temperature and time of the experiment. The activation energy at 50% conversion was estimated to be $\Delta H \sim 155 \text{ kcal mol}^{-1}$ (Fig. 5). Finally, a comparison of Figs. 3 and 4 indicates that the tetragonal phase remained stable to a much higher temperature (~1450°C) in the sintered body than in the loose powder where the conversion was nearly complete at 1450°C. Also, the powder particle size increased gradually with temperature and time.

A similar irreversible tetragonal-monoclinic phase transformation was observed during mechanical grinding of the specimens containing a high percentage of tetragonal phase, as shown in Fig. 6. The as-sintered specimen (Fig. 6a) showed the strong tetragonal 111 peak and a very weak 111 monoclinic peak. When the same specimen was

*The actual critical transition temperature was dependent on a number of factors, e.g. heating rate, sintering time, initial particle size, etc.

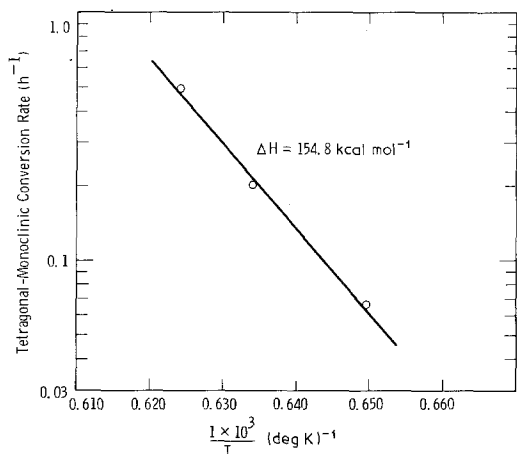
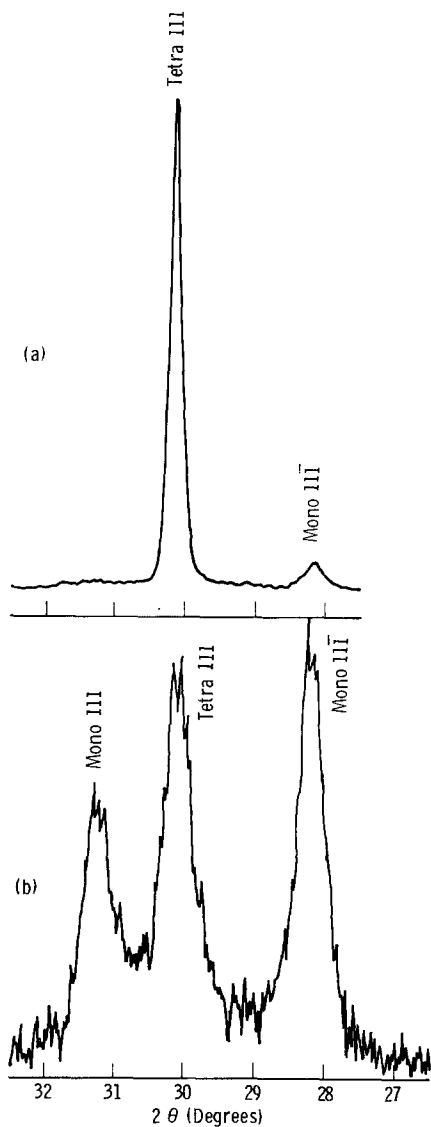


Figure 5 Arrhenius plot of the rate of tetragonal-monoclinic phase transformation versus reciprocal absolute temperature.



powdered by grinding (Fig. 6b), the 111 monoclinic peak appeared and 111 peak became relatively strong. At the same time, the relative concentration of the tetragonal phase was decreased. It is obvious that the martensitic phase transformation occurred by subjecting the specimen to mechanical stress. Such tetragonal-monoclinic phase transformation by mechanical treatment was also observed with powders containing a high percentage of tetragonal phase. Initially, the powders were heat treated at the temperature of annealing of Fig. 4 to obtain high tetragonal phase. On grinding the tetragonal powder, there was a 10 to 15% reduction in tetragonal phase. The results agree well with the data reported by Mitsuhashi *et al.* [4] for powder ZrO_2 .

3.3. Surface versus bulk structure

In the foregoing discussion we have clearly established that sintered bodies containing high concentration of tetragonal phase can be prepared. Since X-ray identification was made on the as-sintered surface and since X-ray has a few microns penetration depth, it is of interest to know whether the surface and the bulk structures are the same. For this, specimens were subjected to careful surface grinding, and after each successive grinding, the ground surfaces were subjected to X-ray analysis for phase determination. Two sets of specimens were selected for analysis; one with an apparent high tetragonal phase and the other with an apparent high monoclinic phase at the outer as-sintered surface. Typical results are plotted in Fig. 7. In Fig. 7a, a specimen (~ 1.5 mm thick) which contained $\sim 90\%$ tetragonal phase at the outer surface is seen to maintain approximately the same composition through half the thickness of the specimen. In contrast, when the specimen contained a high amount of monoclinic phase at the outer surface ($\sim 87\%$ in Fig. 7b), the interior of the specimen was still rich in tetragonal phase under the conditions of heat treatment. There was a sudden rise in tetragonal phase from 13 to 60% at a depth of < 0.1 mm from the outer surface. From these results it can be concluded that the surface and the bulk composition are the same when the specimens show a high amount of tetragonal phase at the outer surface. Secondly, conversion from tetragonal to monoclinic phase during

Figure 6 Effect of grinding on tetragonal-to-monoclinic phase transformation in PSZ ceramic: (a) before grinding, (b) after grinding to powder.

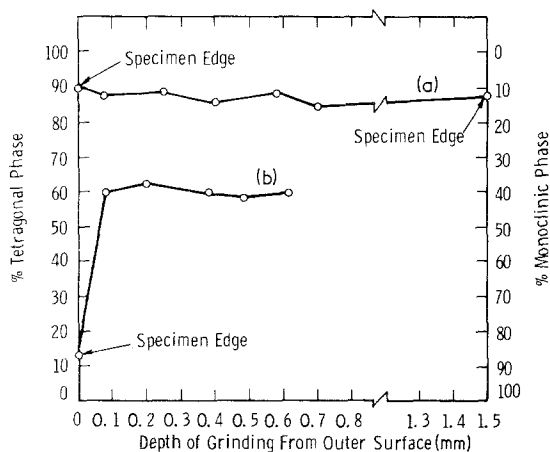


Figure 7 Composition as a function of depth inside the PSZ ceramic (specimen thickness ~ 1.5 mm).

cooling begins at the outer surface. Consequently, specimens containing an apparent high monoclinic phase at the outer surface may still retain a high tetragonal phase in the interior (bulk). This will also explain the presence of surface cracks in the latter specimens.

A further study of the surface versus bulk structure was conducted as follows. Specimens which contained either a high amount of monoclinic phase (80 to 90%) or a high amount of tetragonal phase (82 to 97%) at the outer surface were broken and subjected to X-ray analysis for phase determination. The results are shown in Table II for two sets of four specimens which had comparable densities. Table II also shows the corresponding strength of the specimens and the surface conditions after sintering. The specimens containing an initial high tetragonal phase showed a reduction, while specimens containing an initial high monoclinic phase showed an increment in

tetragonal phase on breaking; there were corresponding changes in monoclinic phase.

The first set of data can be easily explained, in the light of Fig. 7a, by assuming that the composition was rich in tetragonal phase through the bulk of the specimen, and that the act of breaking had caused an increment in monoclinic phase at the fractured surface. This suggests that there is a stress-induced phase transformation in the vicinity of the crack tip. The second set of data can be explained in the light of Fig. 7b. We assume that the composition was rich in tetragonal phase in the interior (say, >60%) and that the transformation to monoclinic phase occurred only at the outer surface during cooling to room temperature. On fracturing and examining the fractured surface, one would thus detect a high tetragonal phase in the bulk compared to that on the surface. On the other hand, if one assumes a high amount of monoclinic phase through the bulk of the specimen, it then becomes impossible to explain the increase in tetragonal phase on fracturing.

3.4. Strength of PSZ ceramics containing tetragonal phase

The PSZ ceramics are unusual in showing not only a stress-induced phase transformation but also a high strength. The individual strength values are shown in Table II. In general, specimens containing high tetragonal phase (as determined by X-ray analysis of the as-sintered surface) routinely showed high strength (3 times as high as the cubic-structured zirconia), whereas specimens containing high monoclinic phase (again, as determined by X-ray analysis of the as-sintered surface) exhibited poor strength in the range of 50 to 100 MPa. Since the latter specimens are believed to contain a

TABLE II Phase characteristics of PSZ ceramics before and after fracturing and corresponding strengths

Sample Number	As-Sintered Surface*		Broken Surface*		Strength (MPa)	Outer Surface Characteristics
	%M	%T	%M	%T		
1st Set of Specimens						
1	3	97	44	56	676	No evidence of microcracks
2	18	82	60	40	683	
3	12	88	59	41	631	
4	3	97	58	42	693	
2nd Set of Specimens						
5	86	14	54	46	224	Evidence of fine network of microcracks
6	89	11	50	50	112	
7	87	13	72	28	30	
8	88	12	50	50	165	

*M = monoclinic. T = tetragonal.

greater amount of tetragonal phase in the bulk (Fig. 7b), the poor strength can be attributed to the presence of a network of fine microcracks at the outer surface, which were formed from the volume change that accompanied tetragonal-to-monoclinic phase transformation. On the other hand, the high strength (~ 700 MPa) of the specimens containing high tetragonal phase could result from the difficulty in initiating the crack, because work has to be done first to cause the phase transformation and then to initiate the crack. The same argument would be true during the propagation of a crack. Part of the energy absorbed during the propagation of a crack will be utilized for the transformation of the metastable phase, thus stabilizing the crack. As a result, the PSZ ceramics containing a tetragonal phase in the structure will exhibit high fracture toughness*. Garvie *et al.* [6] have also noted high strength and high work of fracture of PSZ ceramics containing tetragonal phase, but their structure is claimed to be somewhat different from that observed in the present investigation. They have claimed the dispersion of a metastable tetragonal phase in cubic zirconia. In the present study, no cubic phase was detected and the tetragonal phase was found to be a major and not a dispersed phase. It is believed that the present material is different from other PSZ materials reported in the literature.

4. Conclusions

It is concluded that the tetragonal phase can be made stable in dense polycrystalline partially

stabilized zirconia at temperatures below the equilibrium transformation temperature, by carefully selecting the initial particle size of the powder and the sintering conditions. Transformation to monoclinic phase appears to begin at the outer surface during cooling. Zirconia bodies containing tetragonal phase can undergo stress-induced phase transformation. They are also strong and believed to be tough.

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*A detailed study on this will be described in a separate paper.