

Effect of Overaging on the Room-Temperature Strength of Partially Stabilized Zirconia

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There has been much recent interest in the development of strong, tough zirconia materials for high-temperature structural applications.¹ This preliminary communication is concerned with the influence of aging on the strength, toughness, and phase content of partially-stabilized zirconias (PSZ's). In magnesia-stabilized zirconias (Mg-PSZ's), the strength and toughness increase to a maximum with aging time as tetragonal precipitates develop² and thereafter diminish as the precipitate size increases beyond a critical size³ for spontaneous transformation to the monoclinic phase. This latter decrease in the strength and toughness with aging time is referred to as "overaging". The aging temperature is usually sufficiently high, typically >1400°C, that the kinetic processes may be assumed to have ceased to operate at any subsequent low temperature stage in the specimen history. However, there are applications at intermediate temperatures where this assumption may be in doubt. One such application is the potential use of transformation-toughened ZrO₂ in low-heat-loss diesel engines, where the operating temperature is expected to be in the range 800° to 1000°C. At issue in this particular application is the capacity of the ZrO₂ components to retain their high strength and toughness throughout a nominal lifetime of >5000 h (representative of time between overhauls of heavy-duty trucks).⁴

Accordingly, strength tests were conducted on five commercial PSZ's, one Y₂O₃-stabilized and four MgO-stabilized (Table I). Bar specimens 51 by 3 by 2.2 mm with chamfered edges were machined from the as-received billets. Groups of specimens from each material were heat-treated in a laboratory furnace in air at 1000°C for either 100 or 500 h. All of the specimens thus prepared were broken at room temperature in four-point bending (inner span 9 mm and outer span 27 mm). Two breaks were obtained per specimen, the first from a controlled indentation flaw and the second from the as-machined surface. The indentations were made at a load $P = 100\text{ N}$ in air and were subsequently covered by drop of silicone oil to minimize fatigue effects in the failure mechanics. The bending strengths, σ_f , were evaluated from the breaking loads using simple beam theory.

The phase content of the materials was determined using X-ray diffraction techniques. Since grinding the material into a powder induces the tetragonal→monoclinic phase transformation, the surfaces of the bend specimens were used. These specimens were carefully polished (>50 μm removed) to obtain "bulk material" surfaces. The volume fraction of monoclinic and tetragonal+cubic phases were calculated using integrated intensities of the peaks on the diffractograms.⁵

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Table I. Zirconia Materials Studied

Material	Stabilizer	Amount (wt%)
A*	Y ₂ O ₃	8.1
B†	MgO	3.3
C‡	MgO	4.8
D§	MgO	2.8
E	MgO	2.6

*Sensor material, A.C. Spark Plug Div., General Motors Corp., Flint, MI. †TS grade, Nilsen (U.S.A.) Inc., Glendale Heights, IL. ‡ZT-35, American Feldmeuhle Corp., Hendersonville, NC. §MgO-stabilized TTZ, Coors Porcelain Co., Golden, CO. ||Zircona 2120, Corning Glass Works, Solon, OH.

The results of the breaking tests are shown as a function of heat treatment time in Fig. 1. In these plots individual data points represent mean values of measured strengths for 3 to 5 specimens. The average standard deviation is ±15% for as-machined surfaces and ±7% for the surfaces with the controlled flaws, sufficiently low that the strength trends observed can be considered significant. It is noted that these trends are more or less the same in Fig. 1(A) and (B). Now the strength in the latter case is controlled by the material toughness, K_{Ic} , independent of any explicit dependence on crack dimensions, via the indentation fracture relation^{6,7}

$$\sigma_f = [K_{Ic}^2(H/E)^{1/2}/\eta^4 P]^{1/3}$$

(with P the contact load, H/E the ratio of hardness to elastic modulus, and η a dimensionless constant). It therefore has to be concluded that the strength for the as-machined surfaces must similarly be controlled by the material toughness. This conveniently eliminates the potential complication of extrinsic variables, notably flaw size, from the data analysis.

It is clear from Fig. 1 that the different zirconias respond to the heat treatments in widely different ways. Generally, those MgO-stabilized materials that exhibited high as-received strengths degraded during heat treatment (materials B, D, and E). Material C actually increased in strength for the first 100-h exposure and decreased thereafter. Finally, material A, the Y-PSZ, shows no detectable change in strength over the time range studied.

The volume fraction of monoclinic phase of the bend specimens

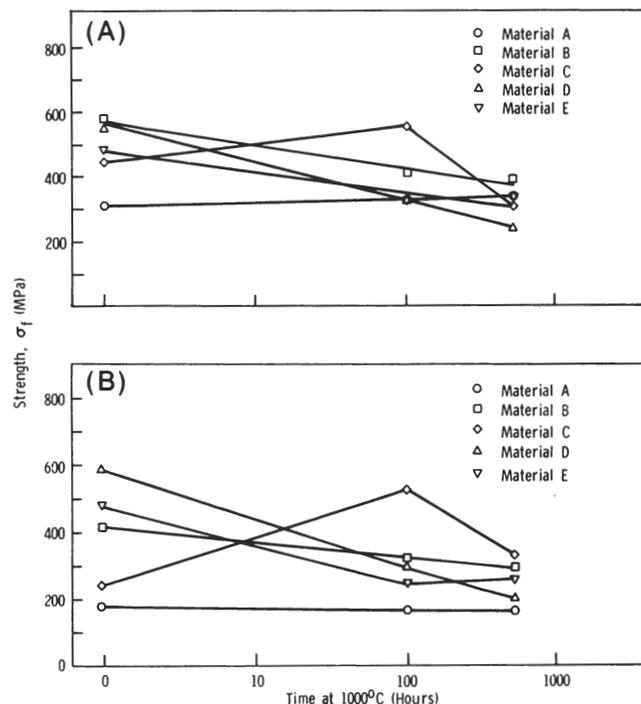


Fig. 1. Strength of ZrO₂ materials for (A) as-machined and (B) indented surfaces as a function of heat-treatment time at 1000°C.

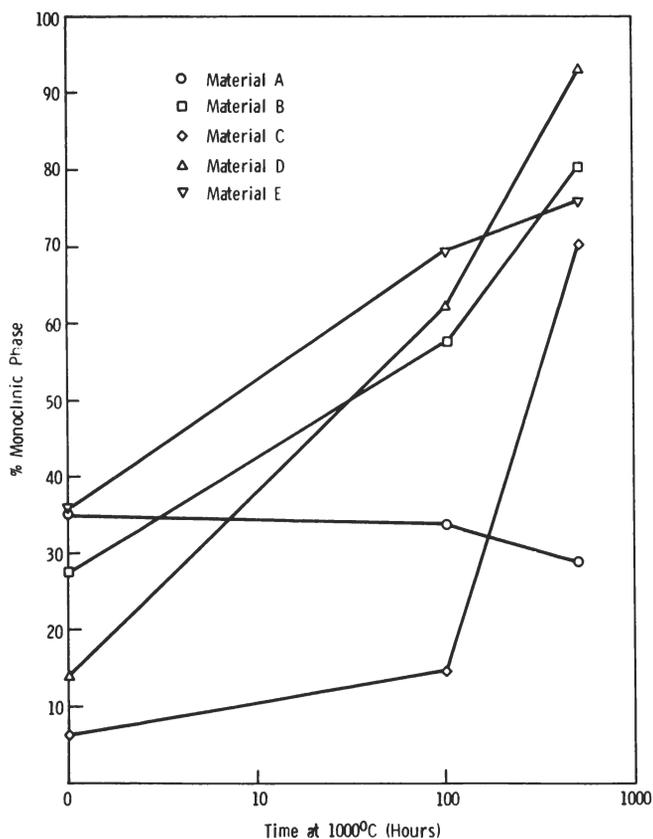


Fig. 2. Fraction of monoclinic phase in ZrO₂ materials as a function of time at 1000°C.

is shown as a function of time-at-temperature in Fig. 2. All the MgO-stabilized samples showed substantial increases in monoclinic content, whereas the phase composition of material A was constant. The three materials that had the highest strengths prior to the heat treatments, materials B, D, and E, showed an approximately linear increase in monoclinic phase content with time-at-temperature. Material C showed a slight increase in monoclinic content after 100 h, followed by a much sharper rise after 500 h.

The loss of strength and toughness is linked to the increase in the amount of monoclinic phase in these materials. This increase in monoclinic ZrO₂ is most likely due to the transformation of the tetragonal precipitates. Our attempts to correlate the phases present with the strength degradation and microstructural changes during aging are in their infancy.⁸ Nevertheless, there are strong implications in the results concerning the performance of candidate zirconias, especially Mg-PSZ, at intermediate temperatures. Thus, in the low-heat-loss diesel engine application, it is conceivable that all the initial benefits of transformation toughening could be lost well before the expiration of the nominal 5000-h working lifetime.

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