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Transformation plasticity and thermoelastic behavior in ZrO₂-containing ceramics

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Résumé.— On passe en revue la plasticité de transformation dans ZrO₂, qui est responsable de la résistance mécanique et de la grande ténacité des nouvelles céramiques à base de ZrO₂. La transformation martensitique tétragonale-monoclinique est un paramètre essentiel, mais il faut une grande maîtrise de la microstructure pour en tirer profit. Dans certaines conditions, cette transformation est réversible, autocatalytique et thermoélastique.

Abstract.— Transformation plasticity in ZrO₂, which is responsible for the high strength and high toughness of advanced ZrO₂-based ceramics, is reviewed. The tetragonal → monoclinic martensitic transformation is of prime importance, but its successful exploitation requires a good deal of microstructural control. Under certain conditions, the transformation can be reversible, autocatalytic, and thermoelastic.

Introduction

Plastic deformation in crystalline solids occurs by the motion of dislocations, twin boundaries, or martensite interfaces.⁽¹⁾ Of these, it is only the martensite case that gives rise to a useful type of plasticity in ceramics at ambient temperatures. In this paper, we review the microstructural control that is necessary to achieve useful mechanical properties in ZrO₂-containing ceramics -- fracture strengths up to ~ 2 GPa and fracture toughnesses up to ~ 18 MPa m^{1/2}.⁽²⁾ These useful properties derive, in one sense or another, from optimized transformation plasticity. We shall also discuss the issue of reversible martensitic transformations under thermoelastic equilibrium, and the conditions under which permanent irreversible transformation can take place.

Crystallography

Useful transformation plasticity in ceramics to date has involved the polymorphism of ZrO₂, whose three crystal structures stable at atmospheric confining pressures are shown in Fig. 1. The high temperature cubic (c) form (space group Fm3m) is isostructural with the mineral fluorite, CaF₂, and in the pure oxide is stable between 2350°C and the melting point at ~ 2800°C. The instability of c-ZrO₂ on cooling below 2350°C is rather surprising, as virtually all other pure oxides* with the fluorite structure do not exhibit polymorphism. This has been attributed⁽³⁾ to the fact that the radius ratio of ZrO₂ is intermediate between that that promotes six-fold coordination in an AO₂ material (TiO₂ structure) and that that promotes eight-fold coordination (CaF₂ structure).

The tetragonal (t) form is a slightly distorted version of the CaF₂ structure (Fig. 1), with a modest tetragonality (c/a ~ 1.02) (space group P4₂/nmc). The strain tensor ϵ_{ij}^t , for the c → t transformation is included in Fig. 1. This

transformation can occur in a displacive but non-martensitic manner in c-Y₂O₃-ZrO₂ alloys;⁽⁴⁾ the high transformation temperature in pure ZrO₂ has prevented detailed study of the transformation. The diffusional precipitation of t-ZrO₂ from supersaturated c-ZrO₂ solid solutions is of great importance, as will be discussed below, but a desire for brevity prohibits further discussion of the c → t transformation(s).

The stable polymorph at low temperature has monoclinic (m) symmetry (P2₁/c space group). As can be seen in Fig. 1, it is a further distortion of the basic fluorite structure, although the components of ϵ_{ij}^m are much larger than those for the c → t transformation. There is general agreement⁽⁵⁾ that this transformation nearly always occurs martensitically, and its occurrence in fine t-ZrO₂ precipitates, dispersed particles, or grains is the basis of useful transformation plasticity in ZrO₂-containing ceramics. The transformation involves a sizeable dilation ($\epsilon_{11} + \epsilon_{22} + \epsilon_{33} \approx 4\%$, as can be seen in Fig. 1), which paradoxically violates Le Chatelier's principle, as the lower temperature phase should be the more dense. Apparently, an increase in the covalent character of the Zr-O bond is associated with the t → m transformation;⁽⁶⁾ as will be discussed below, the dilation improves the mechanical properties, whereas a volume decrease might cause weakening.

Microstructural design and optimization of mechanical properties

The essential ingredient in making strong and tough ZrO₂-containing ceramics is the presence of well-dispersed t-ZrO₂ with an M_s (martensitic start) temperature below room temperature.*

*A variation of this theme occurs in certain dispersion-toughened ceramics such as ZrO₂-toughened Al₂O₃, where microcrack toughening involving already-transformed particles is known to occur.⁽⁷⁾

*Chemically-similar HfO₂ is the only exception.

We will restrict this paper to high ZrO_2 ceramics, which can be divided into PSZ's--partially-stabilized ZrO_2 's (a name with a historic etymology⁽⁸⁾) in which the t- ZrO_2 forms via a precipitation reaction, and TZP's, tetragonal ZrO_2 polycrystals. We will focus on i) Mg-PSZ's, which are based on MgO- ZrO_2 alloys containing 3-4 w/o MgO, ii) Y-TZP's, containing 4-5 w/o Y_2O_3 (these are the two alloy systems which have been put into commercial production) and iii) some experimental ternary MgO- Y_2O_3 - ZrO_2 alloys.

The heat treatment of Mg-PSZ is complex and involved and has been dealt with elsewhere.⁽⁹⁾ Suffice it to say that homogeneous precipitation of t- ZrO_2 from a c- ZrO_2 solid solution is required (Fig. 2a), that Ostwald ripening should be avoided because of the size-dependent M_s temperature,⁽¹⁰⁾ and that a relatively low temperature post-precipitation ("sub-eutectoid"⁽¹¹⁾) heat treatment may be necessary to increase particle transformability under stress and hence increase the maximum toughness. (We have recently discovered⁽¹²⁾ that post-specimen preparation heat treatment is surprisingly also necessary to develop the maximum toughness.) The precipitate microstructure shown in Fig. 2a involves t- ZrO_2 in the form of approximate oblate spheroids but with an exact shape which minimizes both strain and interfacial energies,⁽¹³⁾ set in a c- ZrO_2 matrix in which some $Mg_2Zr_5O_{12}$ (" δ phase") has formed.⁽¹⁴⁾ In the comparable two-phase (c + t) field in the MgO- Y_2O_3 - ZrO_2 ternary, the precipitate morphology differs from that observed in the two binaries⁽¹⁵⁾ and varies with composition; the main factor determining particle morphology is the lattice misfit, which varies with the lattice parameters of the precipitate and matrix. Fig. 3a which will be discussed below, shows plate-shaped t- ZrO_2 precipitates in a c- ZrO_2 matrix in an alloy containing 3 m/o Y_2O_3 and 1 m/o MgO which had been heat-treated for 72 hours at 1450°C.

The microstructures of TZP's are quite different. The solubility of Y_2O_3 in t- ZrO_2 is much larger than is that of MgO, which leads to ceramics in which (nearly) all the grains are t- ZrO_2 with a grain size of $\sim 0.5 \mu m$; such materials (sometimes with Al_2O_3 additions of up to 20 w/o⁽¹⁶⁾) (Fig. 2b), can have strengths in excess of 2 GPa, although the toughness is usually lower than that of Mg-PSZ.

Reversible, autocatalytic, and thermoelastic transformation

It is well-known that surface uplift of a polished surface is the best experimental diagnostic that a martensitic transformation has occurred.⁽¹⁾ This has been used to advantage, initially by Marshall,⁽¹⁷⁾ to follow the occurrence of transformation under load using an optical microscope with Nomarski interference contrast. In the toughest Mg-PSZ's, in which the propensity to transform is so great that stress-strain curves in bending are non-linear and a permanent strain of $\sim 0.1\%$ is achieved prior to fracture, a critical stress exists in which transformation on the grain size scale is reversible; above this stress permanent transformation occurs in apparent shear bands within individual grains, some of which are associated with microcracks; failure occurs not by the propagation of preexisting processing or machining flaws, as in virtually all other ceramics, but by the stable growth and linking together by coalescence of these transformation-induced microcracks.

Shear band formation may be necessary to insure permanent irreversible transformation in these PSZ's, as has been argued elsewhere.⁽¹⁸⁾ Alternatively, the question of reversible versus irreversible transformation in precipitate-toughened systems may involve driving a t/m martensitic interface through an entire particle. Consider Fig. 3a. Under the diffracting conditions chosen for this micrograph, untransformed t- ZrO_2 particles appear white while transformed m- ZrO_2 appear black. Stress-assisted autocatalytic transformation occurred *in situ* in the TEM, due to biaxial stresses accompanying localized electron beam heating. The order of particle transformation is indicated by the lettering. Particle A transformed first and caused the buildup of residual stresses in the foil (see ϵ_{11} from Fig. 1). With further *in situ* loading, particle B transformed, then C, D, etc. The experiment was temporarily halted at the stage represented by Fig. 3a, and the foil taken out of the microscope. Several days later, the foil was returned to the microscope, the area of Fig. 3a was located, and another micrograph taken (Fig. 3b), although with different diffracting conditions. The partially-transformed precipitate H in Fig. 3a had retransformed at some point between recording Figs. 3a and 3b, while particle J had transformed during this interval.

This type of experiment was repeated several times with this alloy,⁽¹⁹⁾ confirming that partially-transformed particles could retransform but fully transformed particles could not. The reversability is intimately associated with the mechanism of particle transformation in this alloy, which is indicated schematically in Fig. 4a and involves "piece-wise" propagation of twin-related martensite variants (the contrast of transformed particles in Fig. 3b is due to these twins). As transformation within a particle proceeds with the propagation of a martensite interface, stress accumulates at the t/ m_1 interface within a particle until a variant of opposite shear (m_2) nucleates and begins to grow and diminish some of the accumulated transformation strains. This process of repeated (piece-wise) nucleation and growth can be reversed if the system is unloaded, and it is not obvious what "stabilizes" a transformed particle against retransformation. High resolution electron microscopy (HREM) by Lee and Heuer⁽¹⁹⁾ (Fig. 4b) revealed, however, that the variant (twin) spacing near the transformed particle/matrix interface is much finer than in the bulk of the particle. This must relieve the residual transformation-induced stresses so effectively that the reverse (m $\rightarrow$ t) transformation cannot be nucleated. (As argued in detail elsewhere,⁽⁵⁾ the ZrO_2 transformation is always stress-induced and nucleation-controlled.)

A different type of reversible and thermoelastic transformation has been observed in similar *in situ* experiments in t- ZrO_2 grains in the as-fired 3:1 alloy of Figs. 3a and 3b prior to the precipitation heat treatment of 1400°C (the firing temperature was 1600°C). The martensite transformation occurs by formation of laths in this case, the laths nucleating at grain (t/t) or interface (c/t) boundaries. If a lath grows completely across a grain, and intersects another boundary, the transformation is not reversible (laths 1 and 2 in Fig. 5a). Stressing by localized electron beam heating again causes nucleation and growth of m- ZrO_2 (lath 3, Fig. 5a), which grows until it impinges a preexisting lath, after which it begins to thicken (Figs. 5b and 5c). Unloading then causes retransformation and shrinkage (Figs. 5d and 5e), leaving finally the original region, with only modest debris to indicate that it had undergone partial transformation.

Conclusions

The martensitic transformation in fine t-ZrO₂ precipitates or grains can be viewed as a special form of transformation plasticity, which in combination with sophisticated microstructural design, has permitted the development of a new family of strong and tough ceramics. In some high ZrO₂ alloys, the transformation occurs under reversible thermoelastic equilibrium, which has been studied in in situ experiments using a finely focussed electron beam to induce biaxial stresses via localized heating.

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REFERENCES

1. J.W. Christian, *Met. Trans* **31A**, 509-538 (1982).

2. M.V. Swain, *Acta Met.* **33** 2083-88 (1985).

3. A.H. Heuer and M. Ruhle, in *Science and Technology of Zirconia II*, edited by N. Claussen, M. Ruhle and A.H. Heuer, The American Ceramic Society, Columbus, Oh., 1984.

4. A.H. Heuer, R. Chaim, and V. Lanteri, *Acta Metall.* **35** (3) 661-666, 1987.

5. A.H. Heuer and M. Ruhle, *Acta Metall.*, **33** (12), 2101-2112, 1985.

6. M. Morinaga, H. Adachi, and M. Tsukuda, *J. Phys. Chem. Solids*, **44**, 301, 1983.

7. M. Ruhle, N. Claussen, and A.H. Heuer, *J. Am. Ceram. Soc.*, **69** (3) 195-197, 1986.

8. E.C. Subbarao, pp. 1-24 in *Science and Technology of Zirconia I*, The Am. Ceram. Soc., Columbus, Oh, 1981.

9. A.H. Heuer, in press, *J. Amer. Ceram. Soc.*

10. A.H. Heuer, N. Claussen, W.M. Kriven and M. Ruhle, *J. Am. Ceram. Soc.* **65** [12] 642-650 (1982).

11. R.H.J. Hannink and R.C. Garvie, *J. Mater. Sci.* **17** 2637-43 (1982).

12. M. Readey, A.H. Heuer, and R. Steinbrech, in press, *J. Am. Ceram. Soc.*

13. V. Lanteri, T.E. Mitchell, and A.H. Heuer, *J. Am. Ceram. Soc.*, **69** (7) 564-69, 1986.

14. R.H.J. Hannink, *J. Mat. Sci.* **18**[2], 457-470, 1983.

15. R.-R. Lee and A.H. Heuer, *J. Am. Ceram. Soc.*, **70** [4] 208-13, 1987.

16. K. Tuskuma, K. Ueda, M. Shimada, *J. Am. Ceram. Soc.*, **68** [1] C4-C5, 1985.

17. D.B. Marshall, *J. Am. Ceram. Soc.*, **69** [3], 173-179, 1986.

18. A.H. Heuer, M. Ruhle, A.G. Evans and D.B. Marshall, to be published.

19. R.-R. Lee and A.H. Heuer, to be published.

Fig. 1 The three polymorphs of ZrO₂ stable at atmospheric confining pressure.

Fig. 2a: TEM bright-field micrograph of t -ZrO₂ precipitates in Mg-PSZ.

Fig. 2b: TEM micrograph of as-fired Y-TZP containing 20% Al₂O₃.

Fig. 3: Sequence of TEM micrographs showing the reversible martensitic transformation of particle H. See text for further discussion.

Fig. 4a: Proposed model for growth of martensitic product by repeated nucleation and limited growth of twin-related variants.
4b: HREM image of fully-transformed particle near particle/matrix interface, showing fine twin spacing.

Figure 5 - Sequence of TEM micrographs showing the thermoelastic martensitic transformation in ZrO_2 . See text for further discussion.