J Mater Sci (2006) 41:7663–7666
DOI 10.1007/s10853-006-0593-7

LETTER

Young's modulus of zirconia at high temperature

**E. Yeugo Fogaing · Y. Lorgouilloux ·
M. Huger · C. P. Gault**

Received: 25 April 2006 / Accepted: 19 June 2006 / Published online: 28 October 2006

Zirconia products can be used in a wide range of engineering applications. The highly refractory nature and good resistance to aggressive environments, such as melted glass, are exploited in the high temperature chemical industry. Structural ceramics take advantage of the well-known possibilities of transformation-toughening. Oxygen probes have been developed because zirconia-based solid solutions exhibit ion conduction. However the polymorphism of zirconia, in particular the transition at about 1170 °C from the low temperature monoclinic phase to the tetragonal phase (stable up to 2370 °C) involves strong volume variations (3–5%) of the unit cell. There is a decrease at the monoclinic–tetragonal transition (M → T) and reciprocally, an increase when cooling down to the reverse transition (T → M below 1000 °C). This expansion involves significant internal stresses in pure polycrystalline zirconia sintered at temperatures higher than $T_{T\rightarrow M}$, which cause drastic cracking on cooling. Therefore the manufacture of large parts of pure monoclinic zirconia is impossible by classical powder densification methods and additives have to be used to stabilize the material in either the tetragonal or cubic phase [1, 2]. However, it was found possible to obtain, using an electro-fused cast process, dense materials (EFZ for electro-fused zirconia) with more than 80 vol.% of pure polycrystalline monoclinic phase embedded into a glassy phase [3] which accommodates the internal stresses. These are caused, either by the thermal expansion mismatches between the phases, or by the volume changes accompanying the transformation of zirconia. The variation of the stress field within this EFZ material can be taken into account by the measurement of the elastic modulus trough a wide temperature range. So, in order to theoretically evaluate this parameter, elastic properties of pure zirconia and those of the glassy phase are required. This letter proposes an evaluation of the elastic properties of pure zirconia in the 20–1400 °C temperature range, starting from literature data for single crystals. This information is then used to interpret experimental variations of Young's modulus versus temperature observed in EFZ.

Very little work is reported in literature on the elastic properties of pure monoclinic zirconia. Elastic constants have been derived by Chan et al. [4], from ultrasonic velocity measurements by Brillouin scattering in monoclinic single crystals, in the 20–1000 °C temperature range. Then, the behaviour of the elastic moduli as a function of temperature of an hypothetic monoclinic polycrystal has been predicted up to 1000 °C by the authors, by using a Voigt–Reuss–Hill (VRH) approach [5]. Furthermore, Mirgorodsky et al. [6] extrapolated these data up to $T_{M\rightarrow T}$ and calculated, by using lattice vibration models, theoretical elastic constants of tetragonal zirconia just before the T → M transformation, i.e. at 1000 °C. Similar calculations are reported by Kisi et al. at 1400 K (1127 °C) [7]. These literature data values are summarized in Table 1.

Even with this information, there are no available experimental values for polycrystalline tetragonal pure zirconia. Therefore we have calculated, by using a VRH approach [5], at 1000 and 1127 °C (1400 K), the

---

E. Y. Fogaing · Y. Lorgouilloux · M. Huger ·
C. P. Gault (✉)
Groupe d'Etude des Matériaux Hétérogènes, ENSCI,
47 avenue Albert Thomas, 87065 Limoges, France
e-mail: c_gault@ensci.fr

Table 1 Elastic properties of monoclinic and tetragonal zirconia at various temperatures

Temperature (°C)		20	300	600	800	1000	1127	1170
Monoclinic polycrystal, after [4–6]	E (GPa)	241	236	235	234	226		218
Tetragonal single crystal, after [6, 7]	C_{11} (GPa)					395	263	
	C_{12} (GPa)					26	15	
	C_{13} (GPa)					105	72	
	C_{33} (GPa)					326	262	
	C_{44} (GPa)					42	55.9	
	C_{66} (GPa)					56	44	
Tetragonal polycrystal, (VRH calculations)	E (GPa)					195.5	190.7	

Young's modulus E of an ideal tetragonal polycrystal from the elastic constants C_{ij} of a tetragonal zirconia single crystal. The result is given at the bottom of Table 1.

One can see that, at 1000 °C, where the two polymorphs of zirconia exist (monoclinic when heating, starting below $T_{M \rightarrow T}$, or tetragonal when cooling from a temperature higher than $T_{M \rightarrow T}$), the Young's modulus of the tetragonal phase is lower than that of the monoclinic phase.

Then, in order to predict the elastic behaviour of EFZ at different temperatures starting from thes values, an analytical equation has been used to describe for the variation of E versus temperature for both monoclinic and tetragonal polymorphs. The plot in Fig. 1 of Young's modulus values reported in Table 1 shows a regular decrease versus temperature for monoclinic zirconia from 20 °C (293 K) up to 1170 °C (1443 K), as usual for oxides. The two points for tetragonal zirconia at 1000 °C (1273 K) and 1127 °C (1400 K) are also plotted in the same figure.

Wachtman et al. proposed an empirical relation for the variations of Young's modulus versus temperature in oxides [8]:

$$E = E_0 - BT\exp\left(-{}^{T_0}\!/_{T}\right) \tag{1}$$

where E is Young's modulus at absolute temperature T, E_0 is Young's modulus at absolute zero, B and T_0 are parameters depending on the material. Indeed, the change of elastic properties versus temperature is an anharmonic property of the crystal. Anderson [9] has shown that, for an oxide crystal at high temperature, T_0 can be approximated by $\theta/2$, where θ is the Debye temperature. Some orders of magnitude of θ are available in literature for yttria–zirconia crystals, unfortunately with some discrepancies: 510 K according to Shirakami et al. [10], 963 K according to Kisi and Yuxiang [11]. No data are reported for pure monoclinic zirconia. Therefore we have plotted the function $E = f(T)$ by adjusting E_0 and B in Eq. 1, for two extreme values of T_0, 255 and 480 K. For each plot, E_0 and B have been adjusted in order to obtain the best fit with data for monoclinic zirconia. The most important result is that the value of T_0 mainly affects the curvature of the curve at low temperature (namely T < 400 K), but that, in each case, Eq. 1 leads to a quasi-linear variation of slope—B above 400 K (Fig. 1, curve 1).

For tetragonal polycrystalline zirconia, assuming that the crystalline anharmonicity is not significantly different between the two polymorphs, the parameters B and T_0 have been considered invariant and E_0 has been adjusted for the best fit (Fig. 1, curve 2) with the

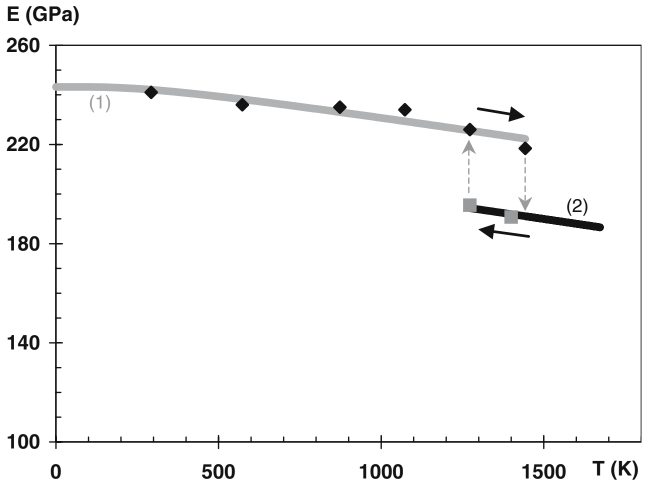

Fig. 1 Young's modulus variations versus absolute temperature T for polycrystalline zirconia: data from Table 1 for monoclinic phase (♦); fit of these data by Eq. 1 with parameters of Table 2 (curve 1); data from Table 1 for tetragonal phase (■); fit of these data by Eq. 1 with parameters of Table 2 (curve 2)

Table 2 Parameters used for calculation of $E = f(T)$ from Eq. 1

Phase	Temp. Range	E_0 (GPa)	B (Gpa K^{-1})	T_0 (K)
Monoclinic	20°C < T < 1170°C (293 K < T < 1443 K)	243.20	0.0202	480
Tetragonal	T > 1000°C (T > 1273 K)	211.96	0.0202	480

two available values, at 1273 K (1000 °C) and 1400 K (1127 °C).

The parameters of Eq. (1) have been determined using a least square analysis to obtain the best agreement between the predicted curve and the E values of Table 1. They are given in Table 2 for the two polymorphs.

Moreover, Fig. 1 clearly shows the hysteresis in the elastic modulus, which characterizes the M–T transition, with a drop on heating and an increase when cooling.

These two analytic expressions for the variation of E versus temperature, during heating and cooling of pure zirconia, has been used to interpret an experimental result obtained in EFZ by in situ measurements of Young's modulus at high temperature with an ultrasonic pulse-echo technique [12]. This material, specially manufactured by Saint-Gobain for this study, is a two-phased one, with 81.5 vol% of monoclinic ZrO_2 combined with an amorphous phase. Figure 2 gives the result of Young's modulus variations versus temperature.

Then, using the variations of the elastic modulus of zirconia (taken from Fig. 1) and those of the amorphous phase (derived from measurements of E versus temperature performed elsewhere on glass samples [13]), a predicted curve for EFZ has been plotted in the same figure. Calculations were performed by using a simple two-phase Hashin–Shtrikman (HS) model, that involves the determination of two bounds for E (E_{HS+} and E_{HS-}), as a function of the elastic properties and of the volume fractions of each phase [14]. It is shown that, in the particular case of stiff particles (here zirconia) embedded in a compliant matrix (here, the glassy phase), E_{HS-} correctly estimates Young's modulus of the material.

The HS approach involves some assumptions that are not strictly achieved in this case, in particular it does not take into account interfacial debonding and cracks into or between constituents, which have been detected by SEM observations [13]. The consequence is that the calculated value of Young's modulus at room temperature is higher (about 10%) than the experimental one. Moreover, the HS calculation was performed by using elastic modulus values measured on glass samples, which were assumed to be of similar composition with the amorphous phase in EFZ. Practically, the presence of impurities involved by the industrial process of EFZ can slightly affect the Young's modulus of the amorphous phase.

Nevertheless, the two curves show a qualitative good agreement for the effect of zirconia phase transition on Young's modulus with a drop at $T_{M \rightarrow T}$ and an increase at $T_{T \rightarrow M}$. Table 3 summarizes the characteristics of the M–T transitions and the effects on Young's modulus, calculated and experimentally observed.

Two remarks on these results can be made:

(i) The values of $T_{M \rightarrow T}$ and $T_{T \rightarrow M}$ taken to draw the curve of Fig. 1 are those corresponding to the thermal expansion anomalies observed in literature, which generally extends over 100 °C [15]. In

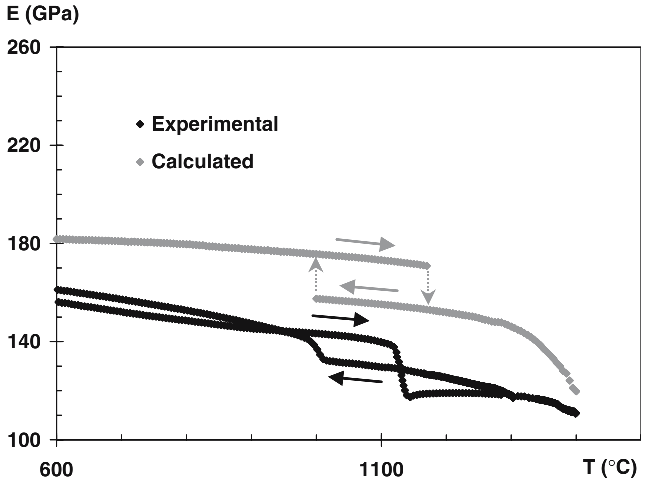

Fig. 2 Young's modulus variations in the range 600–1400°C for EFZ: comparison of experimental result (◆) and calculated result (◆) obtained by using the variations $E = f(T)$ of Fig. 1 for zirconia

Table 3 Temperatures and Young's modulus effects at the monoclinic–tetragonal transitions calculated for pure zirconia (Fig. 1), calculated and measured for EFZ (Fig. 2)

Phase transition	Monoclinic → tetragonal		Tetragonal → monoclinic	
Material	$T_{M \to T}$ (°C)	$\Delta E_{M \to T}$ (Gpa)	$T_{T \to M}$ (°C)	$\Delta E_{T \to M}$ (GPa)
Pure ZrO_2	1170	–31	1000	+31
EFZ (calculated)	1170	–18	1000	+18
EFZ (measured)	1120–1140	–22	1010–980	+10

fact, the M–T transition occurs by a diffusionless shear process, through a temperature range of approximately 1000 °C and describes thermal hysteresis between the heating and cooling cycles, the width of which depends on the size and environment of zirconia particles. In view of this remark, a good agreement is found between experimental values of the temperature transitions derived from Young's modulus measurements in EFZ and values found elsewhere from thermal expansion experiments.

(ii) In EFZ, though the modulus effects caused by intrinsic elastic changes of zirconia are logically predicted by calculation to be symmetric, the amplitude of the drop is significantly greater when heating (–22 GPa), than the amplitude of the increase when cooling (+10 GPa). This is attributed to damage induced in the material by the volume change of zirconia at the M–T transition, which causes, both on heating and cooling, an additional decrease of the average modulus of the material which is superimposed onto the intrinsic modulus effect of the zirconia phase change.

Acknowledgement The authors are grateful to the French Ministry of Industry (MINEFI), which supported this study through the research program PROMETHEREF, and to SAINT-GOBAIN CREE for helpful collaboration, in particular for materials processing.

References

1. Garvie RC (1970) In: Alper AM (ed) High temperature oxides: oxides of rare earths, titanium, zirconium, hafnium, niobium and tantalum, vol. 5, part II. Academic Press, New York and London, p 117
2. Aldebert P, Traverse J-P (1985) J Am Ceram Soc 68(1):34
3. Duvierre G, Boussant-roux Y, Nelson M (1999) Ceram Eng Sci Proc 20(1):65
4. Chan SK, Fang Y, Grimsditch M, Li Z, Nevitt MV, Robertson WM, Zouboulis ES (1991) J Am Ceram Soc 74(7):1742
5. Hearmon RFS (1961) An introduction to anisotropic elasticity. Oxford University Press, Oxford, p 24
6. Mirgorodsky AP, Smirnov MB, Quintard PE (1997) Phys Rev B 55(1):19
7. Kisi EH, Howard CJ (1998) J Am Ceram Soc 81(6):1682
8. Wachtman JB Jr, Tefft WE, Lam DG Jr, Apstein CS (1961) Phys Rev 122(6):1754
9. Anderson OL (1966) Phys Rev 144(2):553
10. Shirakami T, Tojo T, Ataka T, Mori T, Yamamura H (1995) Thermochim Acta 267:415
11. Kisi E, Yuxiang M (1998) J Phys Condens Matter 10(17):3823
12. Huger M, Fargeot D, Gault C (2002) High Temp High pressures 34:193
13. Yeugo Fogaing E (2006) PhD Thesis, University of Limoges, France
14. Hashin Z, Shtrikman S (1963) J Mech Phys Solids 11:127
15. Underwood WA, Thomas EA (1986) Glass Ind 67(10):14