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The size effect of the martensitic transformation in ZrO_2-containing ceramics

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The relationship between the starting temperature of the martensitic transformation, M_s, and the grain size of the parent phase, d, in ZrO_2-containing ceramics was investigated. The experimental results showed that in tetragonal zirconia polycrystals doped with CeO_2 (8 mol%) and Y_2O_3 (0.25 mol%) (8Ce, 0.25Y–TZP), the M_s temperature displays a linear relationship with $d^{-1/2}$, its slope being negative. A new explanation for this phenomenon, the so-called the size effect, has been presented, in which the grain size of the parent phase affects the M_s temperature through the strength of the parent phase. Thermodynamic calculation of the relationship between M_s and d gives a result consistent with the experimental ones.

1. Introduction

Garvie [1] first found that in ZrO_2 powders, there existed a critical crystallite size, d_c, above which the metastable tetragonal phase transforms into the monoclinic phase, m. Hannink *et al.* [2, 3] later found that similar phenomena also existed in CaO partially stabilized zirconia (Ca-PSZ) and zirconia-toughened alumina (ZTA), and that a linear relationship existed between the starting temperature for martensitic transformation, M_s, and the reciprocal of the mean particle size. This relationship was also found in Ce-TZP [4]. The above phenomenon was called the size effect of the martensitic transformations in ZrO_2-containing ceramics (or briefly, the size effect). A long-standing controversy exists in the literature concerning the source of the size effect, and the argument continues. Considering the change of the surface energy and the strain energy before and after the transformation, Garvie *et al.* [1–3, 5–8] thermodynamically calculated the free energy change from the initial tetragonal state to the final monoclinic state, and obtained the relationship between M_s and d^{-1}. In their calculation, the area of the new phase, the angle of lattice cell associated with the t–m transformation and the equilibrium temperature between the two phases, were rather confusing. Evans *et al.* [9] suggested that the energy change of the twin structure is the source of the size effect. They thought that for a grain with a certain grain size, the greater the number of twins in it, the lower was the strain energy. However, twinning can only reduce the shear strain energy, and cannot reduce the constraint of the matrix. Therefore, the critical grain size does not seem to depend on the energy change of the twin structure. Lange [10] proposed that microcracks and/or twins alleviate the constraint of the matrix and therefore reduce the strain energy. But this does not mean that the microcracks and/or twins are the decisive factor in the transformation. It should be pointed out that these authors all confusingly took the whole grain area of the parent phase as the area of the new phase.

Andersson and Gupta [11], Heuer *et al.* [12, 13], and Chen *et al.* [14–16] thought that the martensitic transformation in ZrO_2 was controlled by nucleation. But they did not give a quantitative or semi-quantitative calculation of the relationship between the M_s temperature and the grain size.

In addition Garvie *et al.* [5, 17, 18], using the soft-mode theory, obtained a linear relationship between the M_s temperature and the effective mass in ZrO_2/HfO_2 solid solution. Obviously this is not the size effect mentioned above.

A thermodynamic study of the martensitic transformation in ferrous alloys [19] and copper-based alloys [20] showed that the grain size influences the M_s temperature through its effect on the strength of the parent phase which is the resistance to the martensitic transformation. From this point of view, it was calculated that, in Cu–Zn–Al alloy, the M_s temperature is proportional to $d^{-1/2}$ [20]. Because TZP are also crystalline materials, it is reasonable to believe that the martensitic transformation in TZP ceramics should obey the same rule. Accordingly, the relationship between the M_s temperature and the grain size in Ce, Y–TZP and the nature of the size effect in ZrO_2-containing ceramics, are further studied in this paper.

2. Experimental procedure and results

The experimental material was tetragonal zirconia polycrystals doped with 8 mol % ceria and 0.25 mol %

0022-2461

yttria (8Ce, 0.25Y–TZP). The powder of this composition was obtained by mechanically mixing powders of Y_2O_3 and ZrO_2–CeO_2 prepared by the coprecipitation method. The powders were uniaxially pressed and then hydrastatically pressed, followed by sintering at temperatures from 1400–1600 °C for 2 h. The size of the specimen was about 1.5 mm × 1.5 mm × 12 mm.

The M_s temperatures were measured using an LK-02 dilatameter. Because the M_s temperatures of the materials used were lower than room temperature, liquid nitrogen was used as cooling medium. The M_s temperatures were obtained by drawing tangents at the lowest point on the dilatometry curve. The mean grain size was measured from scanning electron micrographs of the fracture surfaces of the specimens.

Fig. 1 shows some scanning electron micrographs of the TZP with different grain sizes revealing that the grain size increases with increasing sintering temperature.

Fig. 2 shows the linear relationship between the M_s temperature and $d^{-1/2}$ with a negative slope.

3. Discussion

The change in the total free energy per unit volume associated with the martensitic transformation, $\Delta G^{t\to m}$, may be expressed as

$$\Delta G^{t\to m} = \Delta G_c^{t\to m} + \Delta U_{str}^{t\to m} + \frac{S}{V}\Delta\sigma + \Delta G_s \tag{1}$$

where $\Delta G_c^{t\to m}$ and $\Delta U_{str}^{t\to m}$ are changes in chemical free energy and strain energy per unit volume, respectively, $\Delta\sigma$ is the change of the specific surface energy from t to m phase, S is the area of the new phase (m), V is the volume of the grain of the parent phase. ΔG_s is the stored energy in the substructure of the martensite (m). ΔG_c can be approximately expressed as

$$\Delta G_c^{t\to m} = q\left(1 - \frac{T}{T_0}\right) \tag{2}$$

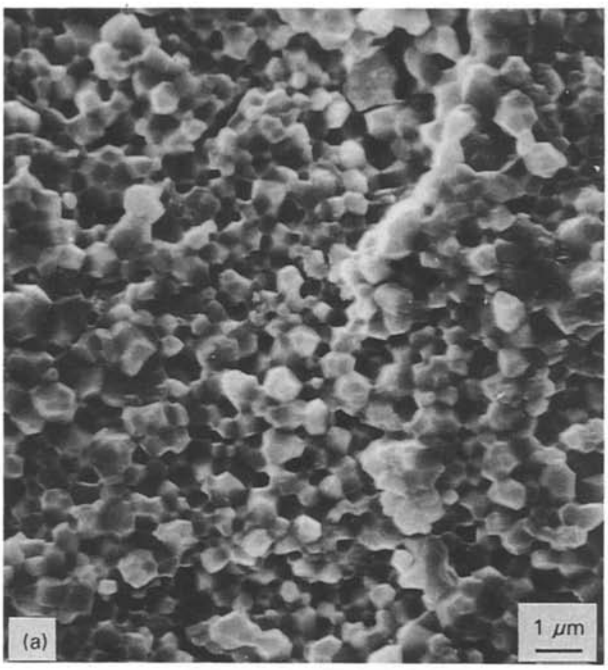
where q is the transformation heat, T is the M_s temperature in the present case, T_0 is the equilibrium temperature between the two phases.

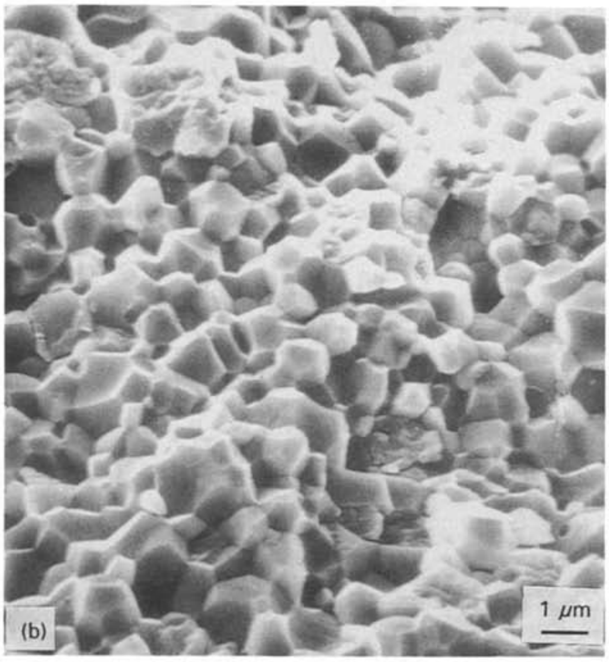
$\Delta U_{str}^{t\to m}$ includes both the change of the shear strain energy, $\Delta U_{shr}^{t\to m}$ and that of dilatational strain energy, $\Delta U_{dil}^{t\to m}$ i.e.

$$\Delta U_{str}^{t\to m} = \Delta U_{shr}^{t\to m} + \Delta U_{dil}^{t\to m} \tag{3}$$

$\Delta U_{shr}^{t\to m}$ and $\Delta U_{dil}^{t\to m}$ can be expressed respectively as

$$\Delta U_{shr}^{t\to m} = \frac{1}{2}\tau\gamma_T \tag{4}$$





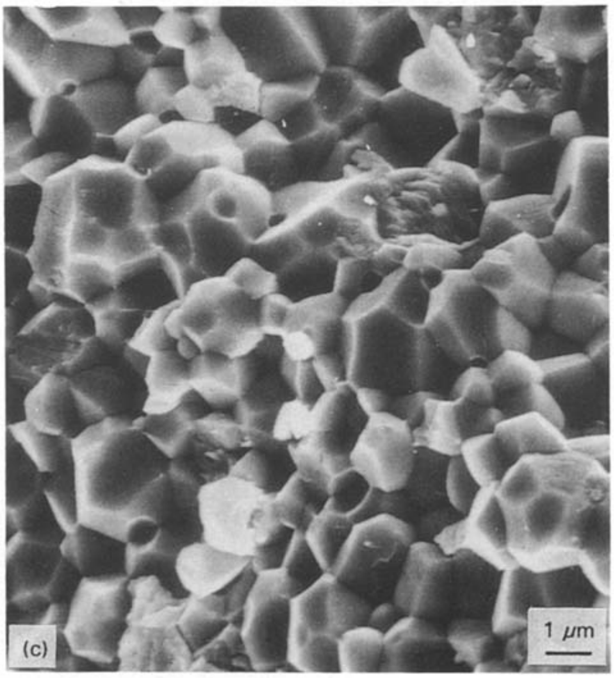


Figure 1 Scanning electron micrographs of the fracture surfaces of 8Ce, 0.25Y–TZP sintered at (a) 1500 °C, (b) 1550 °C, and (c) 1600 °C, for 2 h.

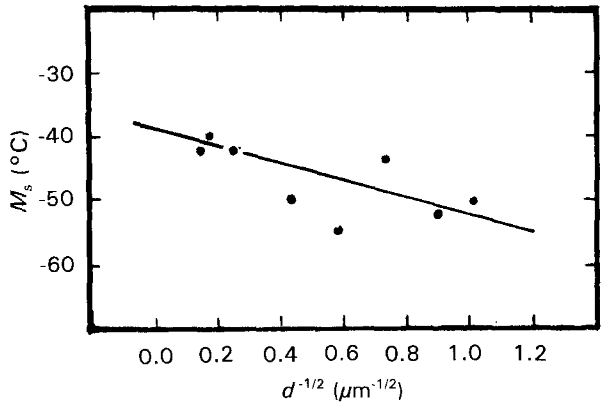


Figure 2 M_s temperature versus grain size in 8Ce, 0.25Y–TZP.

$$\Delta U_{\mathrm{dil}}^{\mathrm{t}\to\mathrm{m}} = \frac{E}{9(1-\nu)}\left(\frac{\Delta V}{V}\right)^2 \qquad (5)$$

where τ is the required critical shear stress, γ_{T} is the transformation strain, E and ν are the elastic modulus and Poisson's ratio of the material, respectively, $\Delta V/V$ is the relative volume change associated with the transformation.

Assuming that when the new phase (m) just grows out, it is a lath of a triangle shape with $d/4$ in height and $d/10$ at the base. The grain of parent phase is a sphere of diameter d. Thus we obtain

$$\frac{S}{V}\Delta\sigma = \left[2\left(\frac{1}{2}\right)\left(\frac{d}{10}\right)\left(\frac{d}{4}\right)\Big/\frac{4}{3}\pi\left(\frac{d}{2}\right)^3\right]\Delta\sigma$$

$$= 0.048\,\frac{\Delta\sigma}{d} \qquad (6)$$

Taking $d = 2\ \mu$m, $\Delta\sigma = 0.36\ \mathrm{J\,m^{-3}}$ [21], from Equation 6, $S/V\ \Delta\sigma$ is found to be $67\ \mathrm{kJ\,m^{-3}}$.

From Equation 4, we obtain

$$\Delta U_{\mathrm{shr}}^{\mathrm{t}\to\mathrm{m}} = \frac{1}{2}\mu\gamma_{\mathrm{T}}^2$$

$$= \frac{1}{2}\left[\frac{E}{2(1+\nu)}\right]\gamma_{\mathrm{T}}^2 \qquad (7)$$

where μ is the shear modulus. Taking $\nu = 0.25$ [6], $E = 200$ GPa, [6, 16] and the angle of the surface relief = 2° [22], then $\gamma_{\mathrm{T}} = 2/90\pi = 0.07$. Substituting these values into Equation 7, $\Delta U_{\mathrm{shr}}^{\mathrm{t}\to\mathrm{m}}$ is found to be $1.96\times10^5\ \mathrm{kJ\,m^{-3}}$.

It can be seen in Equation 1 that the value of $S/V\Delta\sigma$, $67\ \mathrm{kJ\,m^{-3}}$, is so small that it can be neglected. From Equations 1–6, we obtain

$$\Delta G^{\mathrm{t}\to\mathrm{m}} = q\left(1-\frac{T}{T_0}\right) + \frac{1}{2}\tau\gamma_{\mathrm{T}}$$

$$+ \frac{E}{9(1-\nu)}\left(\frac{\Delta V}{V}\right)^2 + \Delta G_{\mathrm{s}} \qquad (8)$$

As a crystalline solid, TZP ceramics may obey the Hall–Petch equation. So the shear strength of the parent phase of the TZP may be expressed as

$$\tau = \tau_0 + kd^{-1/2} \qquad (9)$$

in which τ_0 is the critical shear stress of the single crystal, k is a positive constant related to the material, d is the grain size.

Substituting Equation 9 into Equation 8 gives

$$\Delta G^{\mathrm{t}\to\mathrm{m}} = q\left(1-\frac{T}{T_0}\right) + \frac{1}{2}(\tau_0 + kd^{-1/2})\gamma_{\mathrm{T}}$$

$$+ \frac{E}{9(1-\nu)}\left(\frac{\Delta V}{V}\right)^2 + \Delta G_{\mathrm{s}} \qquad (10)$$

Letting $\Delta G^{\mathrm{t}\to\mathrm{m}} = 0$ and notice $T = M_{\mathrm{s}}$, we have, from Equation 10

$$M_{\mathrm{s}} = \left[1 + \frac{\tau_0\gamma_{\mathrm{T}}}{2q} + \frac{E}{9q(1-\nu)}\left(\frac{\Delta V}{V}\right)^2 + \frac{\Delta G_{\mathrm{s}}}{q}\right]T_0$$

$$+ \frac{k\gamma_{\mathrm{T}}T_0}{2q}d^{-1/2} \qquad (11)$$

and letting

$$M_{\mathrm{s}}^0 = \left[1 + \frac{\tau_0\gamma_{\mathrm{T}}}{2q} + \frac{E}{9q(1-\nu)}\left(\frac{\Delta V}{V}\right)^2 + \frac{\Delta G_{\mathrm{s}}}{q}\right]T_0 \qquad (12)$$

$$K = \frac{k\gamma_{\mathrm{T}}T_0}{2q} \qquad (13)$$

then

$$M_{\mathrm{s}} = M_{\mathrm{s}}^0 + Kd^{-1/2} \qquad (14)$$

When $d \to \infty$, $M_{\mathrm{s}} = M_{\mathrm{s}}^0$, i.e. M_{s}^0 is the starting temperature of the martensitic transformation in a single crystal. Because q is negative, from Equation 13, we can see K is a negative value. So, from Equation 14, it is shown that M_{s} has a linear relationship with $d^{-1/2}$, with a negative slope. This is consistent with the present experimental results (Fig. 2).

Figs 3–5, which are respectively obtained from the data in [4], [6] and [23], show that in Ce–TZP, Ca–PSZ, and $\mathrm{Al_2O_3}$/Ce–TZP, there exists a similar linear relationship between M_{s} and $d^{-1/2}$.

The similarity in the size effect of the martensitic transformation both in metallic alloys and ceramics is

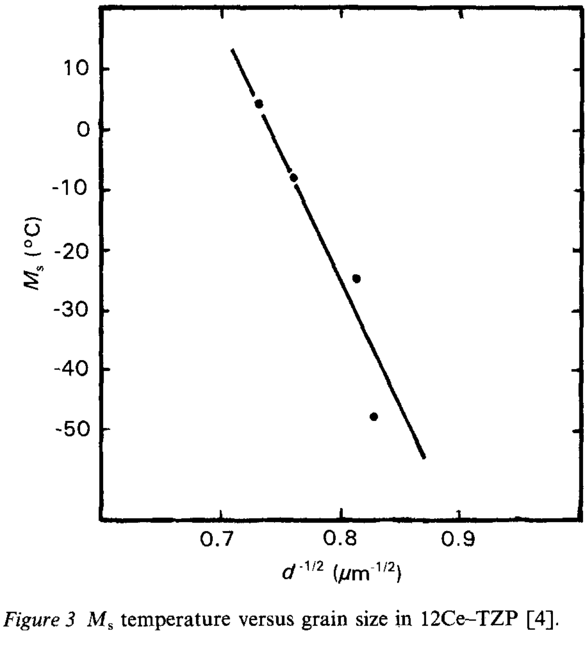


Figure 3 M_s temperature versus grain size in 12Ce–TZP [4].

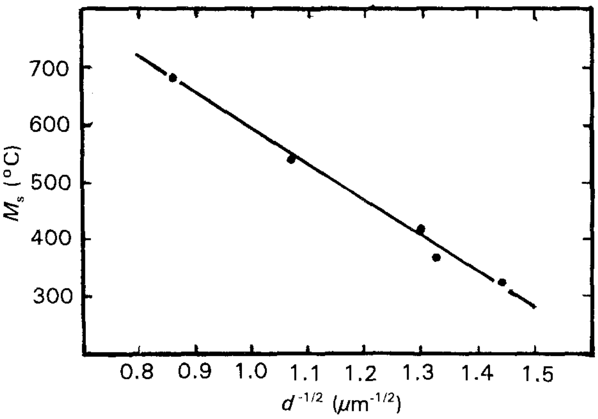


Figure 4 M_s temperature versus grain size in Ca–PSZ [6].

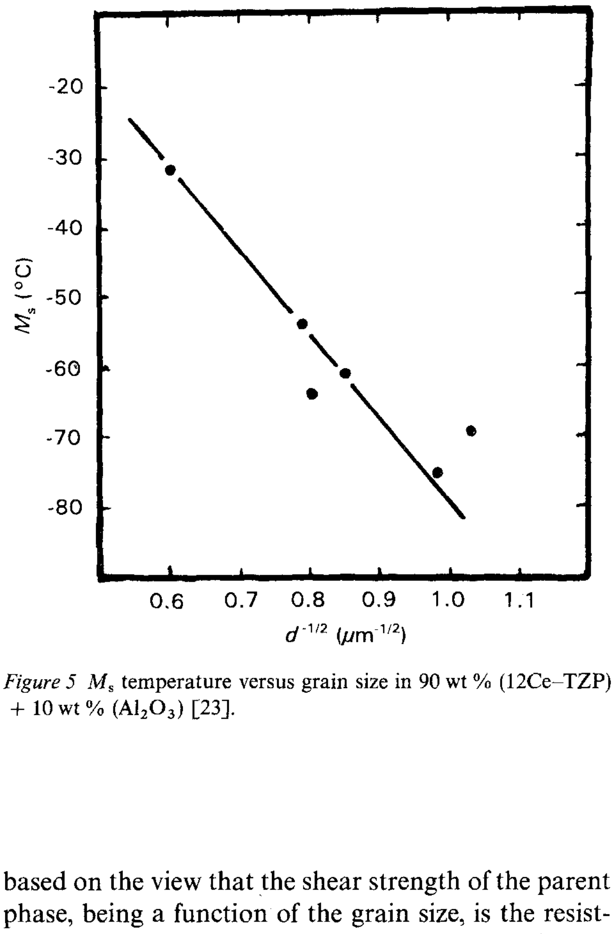


Figure 5 M_s temperature versus grain size in 90 wt % (12Ce–TZP) + 10 wt % (Al_2O_3) [23].

based on the view that the shear strength of the parent phase, being a function of the grain size, is the resistance to the martensitic transformation. Thus the larger the grain size, the lower the shear strength of the parent phase, the higher the M_s temperature will be, and vice versa.

4. Conclusions

The effect of the grain-size effect of the martensitic transformation in the ZrO_2–8 mol % CeO_2–0.25 mol % Y_2O_3 ceramic material was studied. The following conclusions can be drawn.

1. The starting temperature of the martensitic transformation, M_s, has a linear relationship with the reciprocal of the square root of the grain size of the parent phase, d. The relation can be expressed as

$$M_s = M_s^0 + Kd^{-1/2}$$

where M_s^0 is the starting temperature of martensitic transformation in a single crystal, K is a negative constant related to the material.

2. In ZrO_2-containing ceramics, the grain size influences the M_s temperature through the strength of the parent phase, which is the resistance to the occurrence of the martensitic transformation.

Acknowledgement

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