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Grain Size Dependence of the Transformation Temperature of Tetragonal to Monoclinic Phase in $ZrO_2(Y_2O_3)$ Ceramics

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Abstract: The energetics of transformation from tetragonal to monoclinic phase in $ZrO_2(Y_2O_3)$ ceramics are investigated using a thermodynamic approach and an expression for transformation temperature dependence on grain size is proposed. For fully dense $ZrO_2(2\ mol\%Y_2O_3)$ ceramics, a quantitative formula describing the relationship between the starting point of the tetragonal to monoclinic transformation (M_s) and grain size (d) has been derived on the basis of thermodynamic analysis, i.e.

$$M_s = \frac{0.34\times 10^6 d^2 - 5.49\times 10^3 d - 4.97 d^{0.5} - 8.69\times 10^{-3}}{7.34\times 10^3 d^2 + 0.565 d}$$

Experimental results are compared with theoretical predictions and general agreement is found. Factors resulting in some deviation between the experimental and theoretical results are also discussed. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

The tetragonal (t) to monoclinic (m) transformation in ZrO_2 is believed to be one of the effective ways of improving the brittleness and reliability of structural ceramics, which is usually termed transformation toughening. The prerequisite for the occurrence of transformation toughening is the retainment of the high temperature phase to an ambient temperature or below. The stabilization of the tetragonal phase can be achieved using several approaches, e.g. the addition of stabilizers such as Y_2O_3, CaO, MgO and external constraint exerted by a matrix such as Al_2O_3 or mullite. Initiation of the transformation at or below room temperature is critically dependent on the scale of the microstructure, especially the size of grains or inclusions.[1] After many years of intensive research, different formulas have been proposed using different methods to correlate the particle size with the transformation start temperature (M_s) and there are conflicting views on factors contributing to the transformation.[2–5]

It is well documented that the t → m transformation in ZrO_2 is nucleation-controlled,[6] while the transformation in $ZrO_2(Y_2O_3)$ ceramics is controlled by both nucleation and growth and therefore is time-dependent.[7] Previous articles dealing with the size dependence of M_s often over-emphasize one factor and neglect important roles of some other factors. Lange[2] expresses the critical size for constrained particles from the viewpoint of a thermodynamic theory, taking into account the relaxing effect of microcracks and twins concurrent with the transformation. However, it is rather difficult to determine the values of variables contained in the expression, and as a result, the expression has no practical significance. Schmauder[4] and Becher[8] consider the residual stresses as key factors facilitating the nucleation of m-phase in TZP ceramics and derive an expression describing the relationship between M_s and grain size, but this model is difficult to compare with experimental data. Evans[5] also puts forward a theoretical expression based on the assumption that residual strain energy associated with the variants of twins contributes to the existence of a particle size effect. This expression is rather complicated and no confirmation as to its correctness has been obtained. The intent of this artice is to give a basic and thorough understanding of the origin of the particle size effect in the $ZrO_2(Y_2O_3)$ ceramics and to analyse factors influencing the thermodynamics of the transformation by comparing a quantitative prediction of critical transformation conditions with experimental results.

2 THERMODYNAMICS OF THE t → m TRANSFORMATION IN $ZrO_2(Y_2O_3)$ CERAMICS

The tetragonal to monoclinic transformation in $ZrO_2(Y_2O_3)$ ceramics possesses the following features, that is, a first-order, solid-state structural change accompanying the change of strain energy arising from shear or shear-like displacements. The first-order character of the transformation implies the existence of an interface between two phases, as well as volume change and transformation heat. As for $ZrO_2(Y_2O_3)$ ceramics, the M_s point is affected by density as well as grain size and within the precondition of full density, the grain size is comparatively easily controlled. Thus, the t → m transformation can be monitored and utilized for toughening. Phase constituents of the $ZrO_2(Y_2O_3)$ ceramics can be either tetragonal only or dual tetragonal plus monoclinic depending on the yttria content as well as the sintering temperature. In order to understand the possibility of t → m transformation in a given system (ZrO_2–Y_2O_3), it is necessary to consider the thermodynamics of transformation. The prerequisite for the occurrence of the t → m transformation is obviously the decrease of the free energy of the system. The change in free energy of the system, ΔG, can be written as follows:

$$\begin{aligned}\Delta G = &-\Delta G_c V + \Delta E_{\mathrm{str}} V + KV + \Delta U_s S\\ &-\Delta U_l V + \Delta U_{e1} V + \Delta U_{e2} V\\ &-f_T(\Delta E_{\mathrm{str}} + K)V - f_c(\Delta E_{\mathrm{str}} + K)V\\ = &-\Delta G_c V + (1 - f_T - f_c)(\Delta E_{\mathrm{str}} + K)V + \Delta U_s S\\ &-\Delta U_l V + \Delta U_{e1} V + \Delta U_{e2} V \qquad (1)\end{aligned}$$

where ΔG_c is the chemical free energy difference per unit volume between t and m-phase; ΔE_{str} the strain energy per unit volume due to the non-invariant plane strain; K the invariant plane strain energy per unit volume; ΔU_s the change of overall surface energy; ΔU_l the work done per unit volume by tensile stresses; ΔU_{el} and ΔU_{e2} the per unit volume energies needed to form microcracks and twins, respectively; f_T and f_c the coefficients. The transformation occurs only when the free energy change of the system $\Delta G < 0$, which requires supercooling.

ΔG_c is the chemical free energy difference per unit volume (decrease) between t and m-phase and so is the driving force of the transformation. For a given composition, ΔG_c can be expressed using following formula:

$$\Delta G_c = \Delta H^{\mathrm{t}\to\mathrm{m}} - T\Delta S^{\mathrm{t}\to\mathrm{m}} = \Delta S^{\mathrm{t}\to\mathrm{m}}(T_0 - T) \qquad (2)$$

where $\Delta H^{\mathrm{t}\to\mathrm{m}}$ is the transformation heat which is presumed to be temperature-independent. To the temperature at which t and m-ZrO_2 have the same free energy. It is well established that ΔG_c is just a function of composition (solute content) and temperature, with no relation to particle size.

The non-invariant plane strain energy associated with the t → m transformation, ΔE_{str}, can be written as:[9]

$$\Delta E_{\mathrm{str}} = [1/(1-\gamma)]\mu[(e_{11}^T)^2 + 2\gamma e_{11}^T e_{22}^T + (e_{22}^T)^2] \qquad (3)$$

where e_{11}^T, e_{22}^T are the normal strains accompanying the transformation along the X- and Y-axis of unit crystal cell, respectively, μ the shear elastic modulus, γ the Poisson's ratio.

The invariant plane strain energy caused by the t → m transformation, K, can be expressed as follows:[9]

$$\begin{aligned}K = &[\pi(2-\gamma)/2(1-\gamma)]\mu(e_{13}^T)^2 + [\pi/4(1-\gamma)]\mu(e_{33}^T)^2\\ &-[\pi/32(1-\gamma)]\mu\Big\{13\Big[(e_{11}^T)^2 + (e_{22}^T)^2\Big] + 2(16\gamma - 1)e_{11}^T e_{22}^T\\ &-8(1+2\gamma)(e_{11}^T + e_{22}^T)e_{33}^T\Big\} \qquad (4)\end{aligned}$$

where e_{33}^T, e_{13}^T are the normal and shear strain of transformation along Z-axis and Z-plane of unit crystal cell, respectively.

The overall change of the surface energy concurrent with the transformation consists of the surface energy variation between t and m-ZrO_2(ΔU_t), the increase of surface energy caused by the formation of microcracks (ΔU_{cr}), as well as the increase of interface energy caused by the formation of twins (ΔU_{tw}), therefore, ΔU_s can be given:

$$\Delta U_S = \Delta U_t + \Delta U_{cr} + \Delta U_{tw} \qquad (5)$$

ΔU_I is considered to be the work done per unit volume by the tensile stresses. As a result of the anisotropy of the thermal expansion coefficient of the tetragonal cell, residual stresses are expected to be produced from the temperature difference between sintering temperature and room temperature even when no applied stress is exerted. It is quite understandable that the tensile stress component of the residual stress facilitates the t → m transformation because the transformation entails the occurrence of volume dilatation. According to the literature,[8] local mismatch strain arising from the anisotropy of the thermal expansion coefficient can be expressed as $\Delta\alpha \times \Delta T$. In addition, grain boundaries and grain corners are sites of stress concentration. The magnitude of residual stress at a grain boundary increases with increasing values of d/r_{critic} and in this sense, the t → m transformation in $ZrO_2(Y_2O_3)$ ceramics is always stress-assisted even if there is no applied stress. ΔU_I can be given using the following formula:[8]

$$\Delta U_I = 0.5\sigma_{ij}\epsilon_{ij}^T = [0.5\Delta\alpha \times \Delta T \times E \times d/(r_{\text{critic}})]\epsilon_{ij}^T \quad (6)$$

where σ_{ij} refers to the residual stress at grain boundary; $\Delta\alpha$ is the difference between the thermal expansion coefficient along the *c*-axis and that along the *a*-axis of tetragonal ZrO_2, ΔT is the temperature difference, which can be expressed as $\Delta T = T_{\text{str}} - \text{M}_\text{s}$, T_{str} is a critical temperature below which the residual stress is impossible to be relaxed and M_s is a starting temperature for transformation. In actual fact, T_{str} should be a function of grain size. However, for the present, T_{str} is tentatively considered to be constant. r_{critic} is regarded as the critical grain size for spontaneous t → m transformation in $ZrO_2(Y_2O_3)$ ceramics at room temperature, E is Young's modulus and ϵ_{ij}^T is the shear strain for stressless transformation.

Observations have demonstrated that the microcracking and twinning occur more commonly than was recognized previously because of great shear stress and strain during transformation and thermal expansion mismatch among different particles, as well as a pile-up of dislocations at the grain boundary caused by the transformation shear stress. The strain energies arising from the constraint, which oppose further transformation, can be reduced sufficiently by microcracking and plastic deformation (twinning), whereas new surface energies are generated at the same time.

The stress required to nucleate a microcrack by a pileup of dislocations at the grain boundary can be expressed as:[10]

$$\sigma_c = \sigma_0 + \left[\frac{20E\gamma_0}{(1+\gamma)d}\right]^{1/2}$$

$$\approx \left[\frac{29E\gamma_0}{(1+\gamma)d}\right]^{1/2} = K_m d^{-1/2} \quad (7)$$

where σ_c is the grain boundary fracture stress, σ_0 the Peierls stress (neglected here), γ_0 the grain boundary fracture energy, d the ZrO_2 particle diameter, E the Young's modulus, and γ the Poisson's ratio. In eqn (7)

$$K_m = \left[\frac{20E\gamma_0}{1+\gamma}\right]^{1/2}$$

Consequently, the elastic energy per unit volume needed for the onset of microcracking, ΔU_{e1}, can be written as:

$$\Delta U_{e1} = \frac{1}{2}\sigma_c\epsilon_{ij}^T = \frac{1}{2}K_m d^{-1/2}\epsilon_{ij}^T \quad (8)$$

where K_m can be considered as a microscopic stress intensity factor. Likewise, the per unit volume plastic energy which is necessary for the onset of twinning, ΔU_{e2}, can be expressed as:

$$\Delta U_{e2} = 0.5\sigma_y\epsilon_{ij}^T \quad (9)$$

The precondition for the occurrence of twinning is that the critical transformation stress (σ_c^T) must not be less than yield limit of ZrO_2 ceramic (σ_y), that is $\sigma_c^T \geq \sigma_y$. According to the Hall–Petch formula:

$$\sigma_y = \sigma_0 + \left[\frac{\mu b\tau_g}{\pi d}\right]^{1/2} \approx \left[\frac{\mu b\tau_g}{\pi}\right]^{1/2} \cdot d^{-1/2} = K_s d^{-1/2} \quad (10)$$

where b refers to Burger's vector of dislocation, τ_g is the critical shear stress for the mobilization of dislocations.

$$K_s = \left[\frac{\mu b\tau_g}{\pi}\right]^{-1/2} \quad (11)$$

and then

$$\Delta U_{e2} = \frac{1}{2}K_s d^{-1/2}\epsilon_{ij}^T \quad (12)$$

In formula (1), $f_c(\Delta E_{\text{str}} + K)$ and $f_T(\Delta E_{\text{str}} + K)$ indicate the part of the transformation strain energy relaxed through the formation of microcracking and twinning, respectively, and f_T, f_c are coefficients.

If the tetragonal grain is assumed to be in the form of sphere with d as diameter, then

$$V = \frac{1}{6}\pi d^3 \tag{13}$$

$$S = \pi d^2 \tag{14}$$

Substitute formulas (2)–(6), (8), (12)–(14) into formula (1) and when temperature reaches M_s point, the overall change of energy of the system is equal to zero, i.e. $\Delta G = 0$, then we have:

$$- \Delta S^{t\rightarrow m}(T_0 - M_s)d^3 + (1 - f_T - f_c)(\Delta E_{str} + K)d^3 + \Delta U_s 6d^2 - 0.5\Delta\alpha(T_{str} - M_s)Ed/ (r_{critic})\epsilon_{ij}^T d^3 + 0.5K_m d^{-1/2}\epsilon_{ij}^T d^3 + 0.5K_s d^{-1/2}\epsilon_{ij}^T d^3 = 0 \tag{15}$$

Simplifying the above equation, we get:

$$- \Delta S^{t\rightarrow m}(T_0 - M_s)d + (1 - f_T - f_c)(\Delta E_{str} + K)d + 6\Delta U_s - 0.5\Delta\alpha(T_{str} - M_s)Ed^2/ (r_{critic})\epsilon_{ij}^T + 0.5K_m d^{1/2}\epsilon_{ij}^T + 0.5K_s d^{1/2}\epsilon_{ij}^T = 0 \tag{16}$$

then we can obtain the following formula:

$$M_s = \frac{\Delta S^{t\rightarrow m}T_0 d - 6\Delta U_s - (1 - f_T - f_c)(\Delta E_{str} + K)d}{\Delta S^{t\rightarrow m}d + 0.5\Delta\alpha Ed^2/(r_{critic})\epsilon_{ij}^T} + \frac{0.5\Delta\alpha T_{str}d^2E/(r_{critic})\epsilon_{ij}^T - 0.5d^{1/2}(K_m + K_s)\epsilon_{ij}^T}{\Delta S^{t\rightarrow m}d + 0.5\Delta\alpha Ed^2/(r_{critic})\epsilon_{ij}^T} \tag{17}$$

It is obvious from formula (17) that the M_s temperature increases with increasing T_0 which decreases with increasing Y_2O_3 content, therefore, solute content is a predominant factor in determining the M_s point of $ZrO_2(Y_2O_3)$ ceramics. The residual stress resulting from the anisotropy of thermal expansion coefficient is beneficial for the occurrence of the t → m transformation and consequently lifts the M_s point. The effect of microcracking and twinning is very complicated. On the one hand, part of the strain energy accompanying the transformation can be relaxed in this way. It is this arrested microcracking as well as twinning concurrent with the transformation, that allows for the relaxation of a good part of the constraint imposed by other grains and hence of the shear and dilatational strain energies associated with the transformation. On the other hand, energies needed for the formation of both microcracking and twinning inhibit the occurrence of the t → m transformation. The surface energy term, ΔU_s, which is also attributed to the production of microcracks and twins, forms a barrier to the t → m transformation and therefore decreases the M_s temperature.

3 EXPERIMENTAL RESULTS

Powders of zirconia doped with 2 mol% yttria were preformed into pellets at a pressure of 300 MPa, followed by sintering in the temperature range from 1,400°C to 1,600°C for 5 h at atmospheric pressure, during which furnace cooling was employed to ensure that no macrocracking arising from thermal stresses occurred and more than 99.4% theoretical density was achieved. Samples coated with a thin film of gold were observed with S-570 type scanning electron microscope and a linear interception method was adopted to measure the grain size. Grain sizes were taken as the statistical average value of at least 50 grains for each sample. Surface morphologies of sintered specimens, as shown in Fig. 1, indicate that grain size varies from 0.48 μm to 1.45 μm with sintering temperature changes from 1,400°C to 1,600°C and the grain shape seems to tend to be spherical. Thermal expansion analysis (TEA) was performed using a Perkin-Elmer 7 Series Thermal Analysis System with a sample machined to 3 mm × 3 mm × 4 mm. The point at which the tangential line deviates from the expansion curve was defined as transformation temperature. The thermal expansion curves for ZrO_2(2 mol% Y_2O_3) ceramics sintered at different temperatures are shown in Fig. 2, from which variations of the respective transformation temperature with grain size are clearly indicated (A_s and A_f denote starting and ending temperature for m → t transformation during heating, respectively; M_s and M_f refer to starting and ending

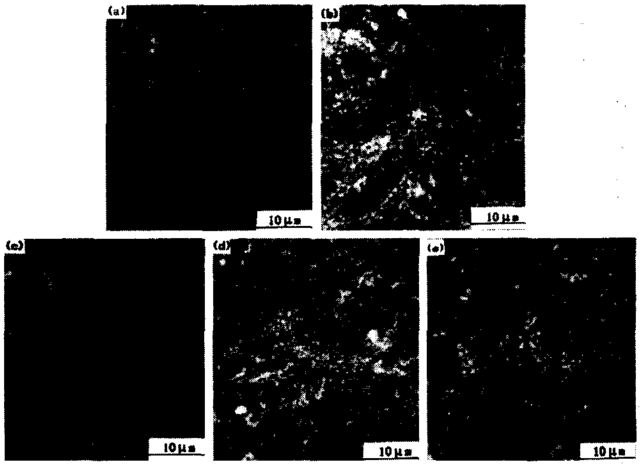

Fig. 1. SEM photographs showing the natural surfaces of ZrO_2(2 mol% Y_2O_3) ceramics at different temperatures: (a) 1600°C; (b) 1550°C; (c) 1500°C; (d) 1450°C; (e) 1400°C.

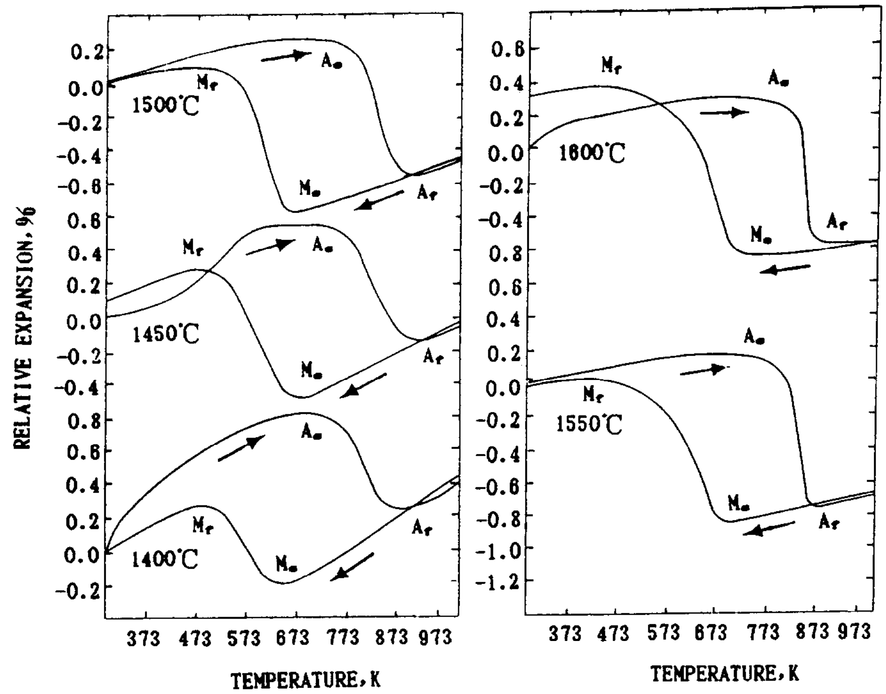

Fig. 2. Thermal expansion curves of ZrO_2(2 mol% Y_2O_3) ceramics sintered at different temperatures.

temperature for t → m transformation during cooling, respectively).

It is evident that the mechanism and energetics of t → m transformation are different in different types of ceramics, largely owing to the diversity of atomic scale structure and chemistry across grain boundaries. In fact, the nucleation of transformation is governed by these conditions. For a given material type and composition, the property of the matrix inevitably plays an important role in the t → m transformation. The shear and dilatational strain energy resulting from the transformation, especially the former, counteract to a great extent the reduction of chemical free energy and constitute an impediment to the nucleation of transformation. The martensitic transformation in ZrO_2(2 mol% Y_2O_3) ceramics will lead to a considerable increase in shear and dilatational strain energy. As a result, the total free energy of the system will be enhanced, which is difficult for nucleation to overcome. Microcracking and twinning have often been observed in stabilizer-containing zirconia ceramics. It is this arrested microcracking as well as twinning concurrent with the transformation, that allows for the relaxation of a good part of the constraint and hence of the shear and dilatational strain energies associated with the transformation, despite the introduction of a new surface energy.

The numerical values of relevant constants used in this calculation are $\gamma = 0.25$,[11] $\Delta H^{t\rightarrow m} = 282.61$ J/cm^3,[12] $e^T_{11} = 0.00412$, $e^T_{22} = 0.01276$, $e^T_{33} = 0.02169$, $e^T_{13} = e^T_{31} = 0.07723$,[12] $\alpha_c = 16.8 \times 10^{-6}$/°C, $\alpha_a = 11.6 \times 10^{-6}$/°C,[8] $f_c = 0.1$, $f_T = 0.3$,[2] $b = 5.2 \times 10^{-10}$ m,[12] $\epsilon^T_{ij} = 0.157$,[13] $\gamma_0 = 2.9$ J/m^2,[3] where γ_0 is the fracture energy of grain boundaries. The equilibrium temperature between t and m-phase, T_0, is presumed to be 500°C according to thermal expansion results. When T_0 is thought to be a function only of yttria content and the effect of grain size is negligible, we have:

$$\Delta S^{t\rightarrow m} = \Delta H^{t\rightarrow m}/T_0 = 0.565\text{J/cm}^3\,{}^\circ\text{C}$$

$$\Delta U_t = \gamma_{t/m} - \gamma_{t/t} = 0.25\text{J/m}^2 - 0.20\text{J/m}^2$$
$$= 0.05\text{J/m}^2 = 5 \times 10^{-6}\text{J/cm}^2\ {}^{12}$$

where $\gamma_{t/m}$ and $\gamma_{t/t}$ indicate the interphase energy between t and m-phase and grain boundary energy of t-phase, respectively.

The interfacial energy term, ΔU_s, consists of surface free energy change between t and m-ZrO_2, U_t; twinning interface energy, ΔU_{tw}; and energy of microcracking formation in ZrO_2, ΔU_{cr}. The numerical values of ΔU_t, ΔU_{tw} and ΔU_{cr} are taken to be 5×10^{-6}J/cm^2, 0.43×10^{-4}J/cm^2,[14] 14×10^{-4}J/cm^2, respectively.[15] Inserting these data into eqn (5) gives:

$$\Delta U_S = 5 \times 10^{-6} + 14 \times 10^{-4}$$
$$+ 0.43 \times 10^{-4} = 14.48 \times 10^{-4}\text{J/cm}^2$$

The Young's modulus of ZrO_2 is reduced by the presence of microcracks in accordance with the expression $E = E_0/(1+1.8Nc^3)$,[13] where E_0 is the Young's modulus of the uncracked material, N the microcracking density, and c the radius of each centre of the microcracking. So E of the microcracked ZrO_2 would be diminished from 220 GPa to 180 GPa as estimated by substituting the appropriate data from Ref. 16. The corresponding shear elastic modulus, μ, is taken to be 72 GPa. With all known parameters, the strain energies represented by formulas (3) and (4), respectively, can be given:

$$\Delta E_{str} = 19.85 \mathrm{J/cm^3},\ K = 1622.5 \mathrm{J/cm^3}$$

Using Lange's[2] research results, 10% of transformation strain energy can be relaxed by way of microcracking and 30% can be relaxed by way of twinning, that is, $f_c = 0.1, f_T = 0.3$. The difference in thermal expansion coefficient for t-ZrO_2 is written as:

$$\Delta\alpha = \alpha_c - \alpha_a = 16.8 \times 10^{-6}/\,^\circ\mathrm{C}$$
$$- 11.6 \times 10^{-6}/\,^\circ\mathrm{C} = 5.2 \times 10^{-6}\,^\circ\mathrm{C}$$

We take $T_{str} = 1{,}000^\circ\mathrm{C}$ as approximation and $r_{critic} = 0.1\ \mu$ m according to literature.[8] In formula (7), the value of K_m can be obtained by inserting the values of E, γ_0 and γ:

$$K_m = \left[\frac{20E\gamma_0}{1+\gamma}\right]^{1/2}$$

$$= \left[\frac{20 \times 180 \times 10^9 \mathrm{Jm^{-3}} \times 2.9 \mathrm{Jm^{-2}}}{1+0.25}\right]^{1/2}$$

$$= 2.88 \times 10 \mathrm{J/cm^{5/2}}$$

then we can get

$$\Delta U_{e1} = \frac{1}{2} K_m d^{1/2} \epsilon_{ij}^T$$

$$= \frac{1}{2} \times 2.88 \times 10 \times 0.157 d^{1/2} = 2.26 d^{1/2}$$

In formula (11), the value of K_s can also be readily calculated using known parameters.

$$K_s = \left[\frac{ubT_g}{\pi}\right]^{1/2}$$

$$= \left[\frac{72 \times 10^{-9} \mathrm{Jm^{-3}} \times 5.2 \times 10^{-10} \mathrm{m} \times 10^3 \times 10^9 \mathrm{Jm^{-3}}}{3.14}\right]^{1/2}$$

$$= 3.14 \times 10 \mathrm{J/cm^{5/2}}$$

where b refers to Burger's vector and is tentatively taken as 5.2×10^{-10}m, T_g indicates the critical stress necessary for the mobilization of dislocations, that is, the maximum stress concentration at the front of dislocation pile-up and is taken as 10^3GPa,[17] then ΔU_{e2} is given

$$\Delta U_{e2} = \frac{1}{2} K_s d^{1/2} \epsilon_{ij}^T$$

$$= \frac{1}{2} 3.14 \times 10 \times 0.157 d^{1/2} = 2.71 d^{1/2}$$

Substituting all the known relevant parameters into formula (17), a quantitative formula describing the relationship between M_s and grain size (d) for ZrO_2(2 mol% Y_2O_3) can be derived:

$$M_s = \frac{9.34 \times 10^6 d^2 - 5.49 \times 10^2 d - 4.97 d^{1/2} - 8.69 \times 10^{-3}}{7.34 \times 10^3 d^2 + 0.565 d} (K) \quad (18)$$

where the unit of d is centimetre.

Formula (18) is illustrated in Fig. 3 in which solid circles and empty circles refer to experimental and calculated values, respectively. The experimental results are in good agreement with calculation, especially at larger grain sizes. The small deviations may be the result of some assumptions and approximations in estimating the relevant parameters, and by not including some other factors that may also affect the transformation, such as particle shape and pre-existing residual stresses. Formula (18) reveals that M_s is a relatively complicated function of grain size (d), but the general trend is that M_s scales with grain size.

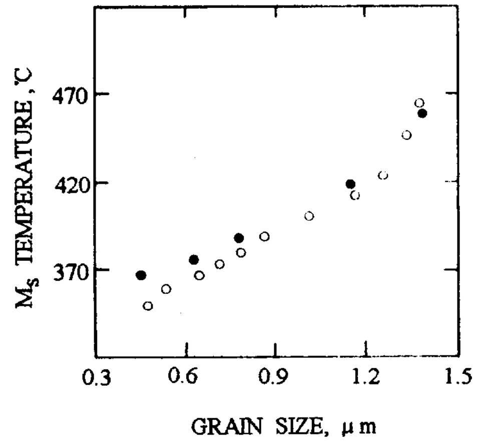

Fig. 3. Comparison of experimental and calculated values of starting temperature of t→m transition (M_s) for sintered ZrO_2(2 mol% Y_2O_3) ceramics. (○) represent the values calculated by using the formula (18) and (●) represent the experimental values measured by the thermal expansion.

4 CONCLUSIONS

1. Factors affecting the t → m transformation energetics of partially stabilized ZrO_2 have been examined. It has been demonstrated that microcracking and twinning are two ways of relaxation of shear and dilatational strain energy accompanying the transformation.
2. For fully dense ZrO_2(2 mol% Y_2O_3) ceramic, quantitative expression of the transformation temperature (M_s) dependence on particle size was derived from energy change considerations after estimating the pertinent energy terms. The expression correlates well with the experimental results.

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