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Transformation toughening

Part 1 *Size effects associated with the thermodynamics of constrained transformations*

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The thermodynamics of the constrained phase transformation is presented with particular reference to size effects introduced by surface phenomena concurrent with the transformation, e.g., the formation of solid–solid surfaces (twins, etc.) and solid–vapour surfaces (microcracks). It is shown that these surface phenomena not only introduce a size-dependent energy term into the total free-energy change, but also reduce the strain energy associated with the transformation, which can result in a transformation at a temperature where $|\Delta G^c|$, the chemical free energy change, is less than U_{se}, the unrelieved strain energy associated with the constrained transformation. The results of this analysis lead to a phase diagram representation that includes the size of the transforming inclusion. This diagram can be used to define the critical inclusion size required to prevent the transformation and/or to obtain the transformation, but avoid one or more of the concurrent surface phenomena.

1. Introduction

It has been shown that a stress-induced phase transformation can be used to increase the fracture toughness of brittle materials based on ZrO_2 [1–5]. Metastable, tetragonal ZrO_2 is the toughening agent. Transformation to its stable, monoclinic structure in the vicinity of the crack front is believed to be responsible for the increased fracture toughness. In fabricating these tougher materials, it has been found that retention of the tetragonal structure at room temperature (or below) is critically dependent on the size of the microstructure. In particular, a critical grain size or inclusion size exists, below which the high-temperature tetragonal phase can be retained and above which retention is not observed.

It would be instructive, from these observations, to determine:

(a) the thermodynamic conditions under which the tetragonal structure can be retained upon cooling from its fabrication temperature;

(b) how the stress-induced transformation contributes to fracture toughness.

In this part, the first part of a series of articles, the theoretical aspects of phase retention will be presented by examining the factors that affect the thermodynamics of a constrained phase transformation. Other articles in this series will address the theory of toughening phenomena and experimental aspects concerned with phase retention and fracture toughness for materials in the ZrO_2–Y_2O_3 and Al_2O_3–ZrO_2 systems.

2. The $ZrO_2(t) \rightarrow ZrO_2(m)$ transformation

Although the succeeding sections are generally applicable for any transformation, the $ZrO_2(t) \rightarrow ZrO_2(m)$ transformation will be used as an example. The tetragonal (t) → monoclinic (m) transformation in this system is athermal, diffusionless and involves both a shear strain and a volume change, for details see the reviews by Subbarao *et al.* [7] and Heuer and Nord [8]. Although some differences of opinion exist, Bailey [9], Bansal and Heuer [10], and more recently, Buljan *et al.* [11] have shown that the orientation relation between the monoclinic and tetragonal (f c c) unit cells is given by $(1 1 0_m) \parallel \{1 0 0_t\}$ and $[1 0 0_m] \parallel [0 0 1_t]$, which can be represented by the "stress-free" or unconstrained strain tensor:

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$$\boldsymbol{\varepsilon}^{\mathrm{t}} = \begin{pmatrix} \dfrac{a_{\mathrm{m}} \cos\left(\dfrac{90-\beta}{2}\right) - a_{\mathrm{t}}}{a_{\mathrm{t}}} & 0 & \tan\left(\dfrac{90-\beta}{2}\right) \\ 0 & \dfrac{b_{\mathrm{m}} - a_{\mathrm{t}}}{a_{\mathrm{t}}} & 0 \\ \tan\left(\dfrac{90-\beta}{2}\right) & 0 & \dfrac{c_{\mathrm{m}} \cos\left(\dfrac{90-\beta}{2}\right) - c_{\mathrm{t}}}{c_{\mathrm{t}}} \end{pmatrix}, \qquad (1)$$

where a, b and c are the cell dimensions of the respective tetragonal (t) and monoclinic (m) structures, and β ($< 90°$) is the monoclinic angle. Substituting the appropriate crystallographic data into Equation 1, it can be shown that the transformation involves a large shear strain (~ 8% and a substantial volume increase (3 to 5%)*.

During cooling, the tetragonal → monoclinic transformation of pure ZrO_2 begins at ~ 1200° C and proceeds over a temperature range (e.g., 1200 to ~ 600° C) until the transformation is complete [6]. Alloying oxides (e.g., Y_2O_3, CeO_2, etc.) lower the transformation temperature. In this regard, the ZrO_2–Y_2O_3 system has been studied. Srivastaba *et al.* [13] have shown that additions of Y_2O_3 to ZrO_2 lower the transformation temperature to 565° C where a eutectoid exists at about 3.5 mol% Y_2O_3. Scott [14] and Stubican *et al.* [15] appear to be in agreement.

3. Thermodynamics of a constrained transformation

Classical theory has shown that retention of the tetragonal structure depends on the magnitude of the strain energy arising from the elastic constraints imposed by surrounding material on shape and volume changes associated with the transformation. Constraint can arise from several sources. First, if the polycrystalline body is single-phase, neighbouring grains, each with a different crystallographic orientation, will constrain the anisotropic strain of one another. Second, the transforming phase can similarly be constrained by a second-phase matrix, as in the case of a two-phase material. The strain energy arising from these contraints can be reduced by microcracking and/or plastic deformation (e.g., twinning). In particular, both microcracking and twinning can accomodate some of the volume- and shape-change associated with the transformation and can reduce the constraint imposed by the surrounding material. Thus, as will be shown, retention of the tetragonal phase not only depends on the elastic properties of constraining material, but also on the possible occurrence of microcracking and/or twinning during transformation.

3.1. Chemical free energy against strain energy

To examine the thermodynamics of the constrained $ZrO_2(t)_2 \rightarrow ZrO_2(m)$ reaction, let us first consider a stress-free, spherical inclusion of the tetragonal phase embedded within a matrix material, as shown in Fig. 1a. On transforming to its monoclinic phase†, a state of stress arises within both the transformed inclusion and the surrounding matrix because of the constrained volume and shape changes. The differential free energy, $\Delta G_{\mathrm{t}\rightarrow\mathrm{m}}$, between these two states per unit volume of transformed material is

$$\Delta G_{\mathrm{t}\rightarrow\mathrm{m}} = G_{\mathrm{m}}^{\mathrm{c}} - G_{\mathrm{t}}^{\mathrm{c}} + U_{\mathrm{se}}^{\mathrm{m}} - U_{\mathrm{se}}^{\mathrm{t}} + U_{\mathrm{S}}^{\mathrm{m}} - U_{\mathrm{S}}^{\mathrm{t}} \qquad (2)$$

or

$$\Delta G_{\mathrm{t}\rightarrow\mathrm{m}} = -\Delta G^{\mathrm{c}} + \Delta U_{\mathrm{se}} + \Delta U_{\mathrm{S}}, \qquad (3)$$

where ΔG^{c} is the chemical free energy (dependent on temperature and composition), ΔU_{se} is the strain energy associated with the transformed particle (for the case considered here $U_{\mathrm{se}}^{\mathrm{t}} = 0$ and

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*The crystallographic data of Pratil and Subbarao [12] can be extrapolated to room temperature to show that the volume increase changes from 3% at 1150° C to 4.5% at room temperature; β is relatively insensitive to temperature.

†It is assumed throughout this paper that the whole inclusion transforms in a spontaneous and uniform matter. Although this assumption neglects the conditions for the nucleation and growth usually associated with these transformations, it does allow us to examine the limiting condition concerning the thermodynamic stability of the constrained inclusion.

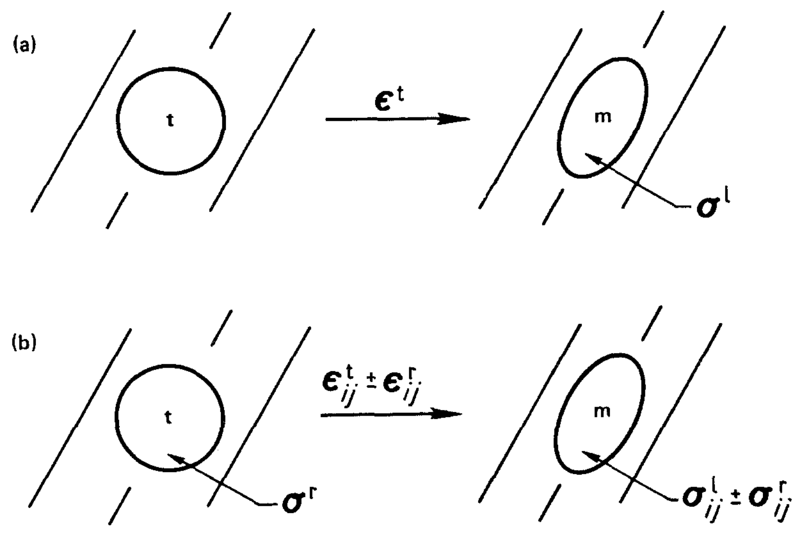

Figure 1 (a) Constrained transformation where the initial state (t) is stress-free and (b) initial state under residual stress, σ_r.

$\Delta U_{se} = U^{m}_{se}$) and surrounding matrix which is usually less senstive to temperature and composition changes, and ΔU_S is the change in energy associated with the surface of the inclusion.

The condition for the transformation requires that $\Delta G_{t \to m} \leqslant 0$, or, from Equation 3*

$$|\Delta G^{c}| \geqslant U^{m}_{se} + \Delta U_S. \tag{4}$$

It can be seen that, since U^{m}_{se} is always positive, the constrained transformation temperature will be different from that for the unconstrained case ($|\Delta G^{c}| \geqslant U_S$). For ZrO_2, constraint lowers the transformation temperature.

The magnitude of the strain energy will depend on the elastic properties of the transformed inclusion and the surrounding matrix, the inclusion shape, and the transformation strain. Eshelby [16] has shown that

$$U^{m}_{se} = \tfrac{1}{2}\sigma^{I}_{ij}\epsilon^{t}_{ij}, \tag{4}$$

where σ^{I} defines the uniform stress state within the transformed inclusion, and ϵ^{t} is the "stress-free" transformation strain [e.g., given by Equation 1 for $ZrO_2(t) \rightarrow ZrO_2(m)$].

The effect of the elastic properties of the constraining matrix can be examined by assuming that the transformation only involves an isotropic volume expansion, $\epsilon^{t}_{ij} = \frac{1}{3}\Delta V/V$. With this assumption it can be shown that, for the case of a sphere,

$$U^{m}_{se} = \frac{k}{6}\left(\frac{\Delta V}{V}\right)^{2}, \tag{6}$$

where

$$k = \frac{2E_1E_2}{(1+\nu_1)E_2 + 2(1-2\nu_2)E_1} \tag{7}$$

and E_1 and E_2 and ν_1 and ν_2 are the Young's moduli and Poisson's ratios of the matrix (1) and transforming particle (2), respectively. That is, the greater the elastic modulus of the constraining matrix, the greater the strain energy and, thus, the lower the potential transformation temperature. For ZrO_2, the constrained transformation temperature will be inversely proportional to the rigidity of the constraining matrix†.

Alloy additions that lower the unconstrained transformation temperature (i.e., additions such as Y_2O_3 that decrease $|\Delta G^{c}|$) will also lower the constrained transformation temperature.

3.2. Effect of residual stresses

In Section 3.1. it was assumed that the initial tetragonal state was free of residual stresses. This is not the normal situation since residual stresses will arise during fabrication (e.g., during cooling from the fabrication temperature as a result of thermal expansion mismatch with the matrix phase). As will be shown, these residual stresses will either increase or decrease the strain energy

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*Throughout this paper, only temperatures where ΔG^{c} is negative are considered; thus, $-\Delta G^{c}$ is written as $|\Delta G^{c}|$, for convenience.

†It should be pointed out that the strain energy term in Equation 3 is only significant for reactions involving relatively small changes in chemical free energy (< several kcal mol^{-1}). It is usually neglected for most chemical reactions where $|\Delta G^{c}| \gg \Delta U_{se}$.

term in Equation 3 and thus will influence the potential transformation temperature.

Fig. 1b illustrates the spherical tetragonal inclusion in a state of residual stress and in its transformed, monoclinic state. The residual stress state is defined by $\boldsymbol{\sigma}^{\mathrm{r}}$ which, according to Eshelby, arises from a "stress-free" strain $\boldsymbol{\varepsilon}^{\mathrm{r}}$, for example, the strain an unconstrained inclusion would exhibit due to thermal contraction. The strain energy associated with the tetragonal state is

$$U_{\mathrm{se}}^{\mathrm{t}} = \tfrac{1}{2}\boldsymbol{\sigma}_{ij}^{\mathrm{r}}\boldsymbol{\varepsilon}_{ij}^{\mathrm{r}}. \tag{8}$$

Using the principle of superposition, it can be shown that the strain energy in the transformed, monoclinic state is

$$U_{\mathrm{se}}^{\mathrm{m}} = \tfrac{1}{2}(\boldsymbol{\sigma}_{ij}^{\mathrm{I}} \pm \boldsymbol{\sigma}_{ij}^{\mathrm{r}})(\boldsymbol{\varepsilon}_{ij}^{\mathrm{t}} \pm \boldsymbol{\varepsilon}_{ij}^{\mathrm{r}}), \tag{9}$$

where $\boldsymbol{\sigma}^{\mathrm{I}}$ and $\boldsymbol{\varepsilon}^{\mathrm{t}}$ are those stresses and strains defined earlier for the transformation from an unstressed tetragonal particle. The ± sign in front of the residual stress/strain terms in Equation 9 arises because the individual components of these tensors can have either the same sense (+) or the opposite sense (−) relative to the components associated with the transformation.

The free-energy change associated with the transformation shown in Fig. 1b is

$$\Delta G_{\mathrm{t}\to\mathrm{m}} = -\Delta G^{\mathrm{c}} + U_{\mathrm{se}}^{\mathrm{m}} - U_{\mathrm{se}}^{\mathrm{t}} + \Delta U_{\mathrm{S}}. \tag{10}$$

Substituting Equations 8 and 9 into Equation 10 gives

$$\Delta G_{\mathrm{t}\to\mathrm{m}} = -\Delta G^{\mathrm{c}} + U_{\mathrm{se}}^{0} \pm \boldsymbol{\sigma}_{ij}^{\mathrm{I}}\boldsymbol{\varepsilon}_{ij}^{\mathrm{r}} \pm \boldsymbol{\sigma}_{ij}^{\mathrm{r}}\boldsymbol{\varepsilon}_{ij}^{\mathrm{t}} + \Delta U_{\mathrm{S}}, \tag{11}$$

where U_{se}^{0} is the strain energy defined by Equation 5 for the case where the tetragonal particle is initially stress-free.

Equation 11 illustrates that the residual stress and strain fields either increase or decrease the strain energy depending on their sense. That is, if the transformational fields are compressive and the initial residual fields are tensile, the strain energy is diminished. If, on the other hand, the residual field has the same sense as the transformational field, the strain energy is increased. This latter case will decrease the transformation temperature.

4. Effect of inclusion size

As mentioned in Section 1, experiments have shown that the retention of tetragonal ZrO_2 is size-dependent. That is, a critical inclusion/grain size exists, below which retention can be achieved and above which it cannot. This size effect cannot be explained by the approach discussed above; what is required is a term in the free-energy expression (Equation 3) which takes account of the size of the transforming volume.

4.1. Influence of ΔU_{S}

The change in the surface energy per unit volume, V, of a transformed spherical inclusion can be expressed as

$$\Delta U_{\mathrm{S}} = \frac{A_{\mathrm{m}}\gamma_{\mathrm{m}} - A_{\mathrm{t}}\gamma_{\mathrm{t}}}{V} = \frac{6(\gamma_{\mathrm{m}} - g_{\mathrm{s}}\gamma_{\mathrm{t}})}{D}, \tag{12}$$

where A_{m} and A_{t} are the interfacial surface areas, γ_{m} and γ_{t} are the specific interfacial surface energies in the transformed and untransformed states, V ($V = \pi D^3/6$) is the transformed volume, D is the diameter of the transformed inclusion and $g_{\mathrm{s}} = A_{\mathrm{t}}/A_{\mathrm{m}}$. Substituting Equation 8 into Equation 9 and rearranging, it can be seen that the surface-energy term introduces a size effect, i.e., a critical particle size, D_{c}, above which the energetics of the transformation are statified (such that $\Delta G_{\mathrm{t}\to\mathrm{m}} \leqslant 0$) and the transformation can proceed,

$$D \geqslant D_{\mathrm{c}} = \frac{6(\gamma_{\mathrm{m}} - g_{\mathrm{s}}\gamma_{\mathrm{t}})}{[|\Delta G^{\mathrm{c}}| - \Delta U_{\mathrm{se}}]}. \tag{13}$$

Garvie [17, 18] has used a similar argument to explain the experimental observation that unconstrained tetragonal ZrO_2 powders are obtained at room temperature when produced with a particle size less than 30 nm. In order to explain this size effect with the surface energy term, it was necessary to assume that $\gamma_{\mathrm{m}} > g_{\mathrm{s}}\gamma_{\mathrm{t}}$*. Based on this assumption and the condition that $\Delta U_{\mathrm{se}} = 0$ for the case of unconstrained powders, the critical particle size, D_{uc}, for the unconstrained powder is

$$D_{\mathrm{uc}} = \frac{6(\gamma_{\mathrm{m}} - g_{\mathrm{s}}\gamma_{\mathrm{t}})}{|\Delta G^{\mathrm{c}}|}. \tag{14}$$

Substituting Equation 14 into Equation 12 and rearranging, the critical size for the constrained

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*Garvie [17, 18] neglected the possibility of internal surface (twins) in the transformed particles which would have produced the same effect without the assumption that $\gamma_{\mathrm{m}} > \gamma_{\mathrm{t}}$.

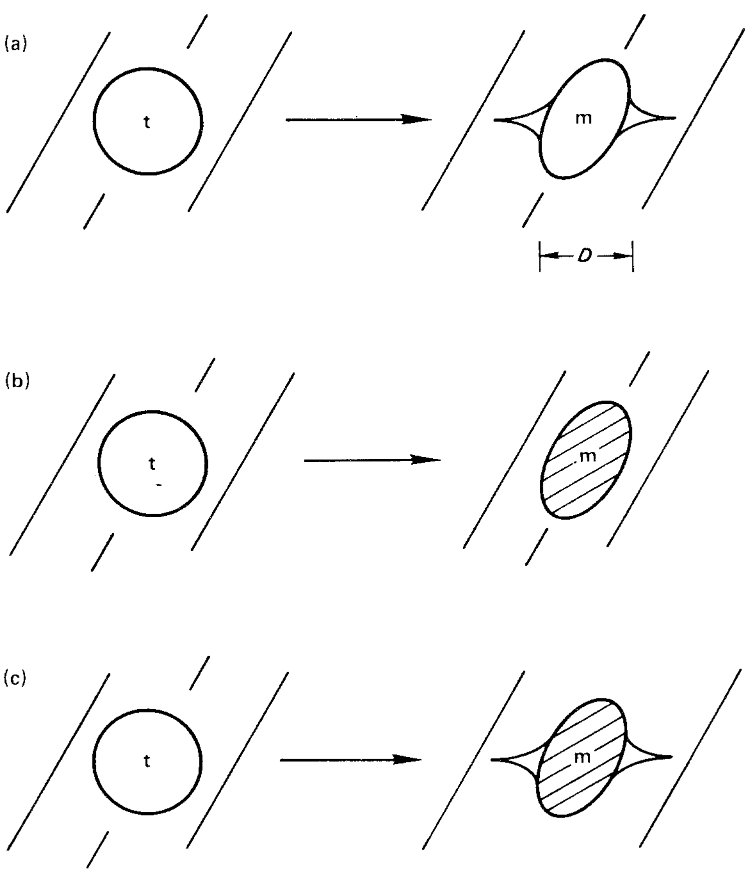

Figure 2 (a) Transformation + microcracking, (b) transformation + twinning and (c) transformation + microcracking + twinning.

state can be related to the critical size for the unconstrained state by

$$D_c = \frac{D_{uc}}{1 - \dfrac{\Delta U_{se}}{|\Delta G^c|}}. \qquad (15)$$

Examination of Equation 15 shows that a critical size does exist when $|\Delta G^c| > \Delta U_{se}$ and that $D_c > D_{uc}$.

4.2. Losss of constraint through microcracking and twinning

As mentioned above, both microcracking and twinning can accompany the $ZrO_2(t) \to ZrO_2(m)$ transformation. Microcracking and twinning both relieve some of the constraint associated with the volume and shape changes, respectively. In both cases, relief of constraint decreases the strain-energy associated with the transformation. As will be shown, the occurrence of microcracking and/or twinning results in a size-effect for cases when $|\Delta G^c| < \Delta U_{se}$.

Let us first consider the case of microcracking. Assume that, during transformation, a small flaw at the inclusion–matrix interface extends and becomes an arrested microcrack, as shown in Fig. 2a (the growth requirements for such a crack are considered in [19–22]). A radial crack would be a likely type of crack due to the volume expansion associated with the transformed ZrO_2 inclusion. The presence of the crack will change the energetics of the transformed particle in two respects. First, the crack will relieve a fraction $(1 - f_c)$ of the strain energy, ΔU_{se}, associated with the uncracked, transformed system. Second, the crack introduces new surface.

The change in free energy of this microcracked system can be written as

$$\Delta G_{t\to m} = -\Delta G^c + \Delta U_{se} f_c + \frac{A_c \gamma_c}{V} + \Delta U_S, \qquad (16)$$

where the $A_c\gamma_c/V$ term in Equation 16 is the energy per unit volume of transformed material associated with the crack surface; A_c is the area of the crack surfaces, γ_c is the fracture energy per unit area and V is the volume of the particle. By defining the area of the arrested crack with respect to the surface of the inclusion ($A_c = \pi D^2 g_c$) and using $V \simeq 6\pi D^3$, Equation 16 can be rewritten as

$$\Delta G_{t\to m} = -\Delta G^c + \Delta U_{se} f_c + \frac{6\gamma_c}{D} g_c + \frac{6(\gamma_m - g_s\gamma_t)}{D}. \quad (17)$$

Both f_c and g_c are numerical values that depend on the size of the arrested crack. Previous work [21, 22] has shown that f_c and g_c are weak functions of the initial flaw size responsible for the extended microcrack.

Equation 17 shows that the size of the transformed particle is now contained in two terms, i.e., one associated with the energy due to the crack and the other associated with the energy due to the surface of the inclusion. Again, the transformation will only proceed when $\Delta G_{t\to m} \leqslant 0$ which, from rearranging Equation 17, defines a critical size for transformation and microcracking:

$$D \geqslant D_c^c = \frac{6[\gamma_c g_c + \gamma_m - g_s\gamma_t]}{|\Delta G^c| - \Delta U_{se} f_c}. \quad (18)$$

Examination of Equation 18 shows that the size effect for transformation and microcracking exists when $|\Delta G^c| > \Delta U_{se} f_c$.

Let us now consider the conditions for transformation and twinning (Fig. 2b). In a manner similar to that discussed for microcracking, the energetics of the constrained transformation in which the transformed particle forms twins can be written as

$$\Delta G_{t\to m} = -\Delta G^c + \Delta U_{se} f_T + \frac{6\gamma_T g_T}{D} + \Delta U_S. \quad (19)$$

where the $6\gamma_T g_T/D$ term is the energy of the twin surface per unit volume of transformed material and the total area of the twin boundaries, A_T, is normalized by the surface of the area of the particle ($g_T = A_T/\pi D^2$); the factors f_T and g_T are dimensionless values, $f_T < 1, g_T > 0$ and γ_T is the twin boundary-energy per unit area.

Similar in all respects to the microcracking phenomena, a critical particle size exists, above which transformation and twinning is possible:

$$D \geqslant D_c^T = \frac{6(\gamma_T g_T + \gamma_m - g_c\gamma_t)}{|\Delta G^c| - \Delta U_{se} f_T}. \quad (20)$$

Again, this size effect only exists for the condition $|\Delta G^c| > \Delta U_{se} f_T$.

Now let us consider the case where both microcracking and twinning accompany the transformation, as shown in Fig. 2c. By using the same approach, it can be shown that a critical inclusion size exists, above which transformation, microcracking and twinning are possible:

$$D \geqslant D_c^{c,T} = \frac{6(\gamma_c g_c + \gamma_t g_t + \gamma_m - g_s\gamma_t)}{|\Delta G^c| - \Delta U_{se} f_c f_T}. \quad (21)$$

Similarly, the condition where this size effect will be observed is $|\Delta G^c| > \Delta U_{se} f_c f_T$.

5. Discussion

The classical theory of constrained phase transformations, as outlined in the first part of this paper, has shown that the potential for lowering the transformation temperature primarily resides with the magnitude of the strain energy that would arise if the transformation were to proceed. For a given transformation, the strain energy depends on the elastic properties of the constraining matrix and the residual strains that pre-exist in the untransformed state. The strain energy can be maximized by maximizing both the elastic properties of the constraining matrix and the pre-existing residual strains which must have the same sense as the transformational strains. Residual strains of opposite sense decrease the strain energy. For the case of ZrO_2, the ideal constraining matrix would not only have a high elastic modulus, but a higher thermal expansion coefficient than tetragonal ZrO_2.

The constrained transformation temperature can also be decreased by decreasing the change in chemical free energy, $|\Delta G^c|$. This can be accomplished by alloying with an additive (e.g., Y_2O_3, CeO_2, etc.) that is known to decrease the unconstrained transformation temperature.

In addition to these more classical results, it has been shown that the thermodynamics of the constrained transformation depend on the size of the transforming volume. This size-effect is introduced through surface changes associated with the transformation. Three different surface related phenomena, microcracking, twinning and microcracking combined with twinning, have the potential for producing a size-effect for conditions where $|\Delta G^c| \leqslant \Delta U_{se}$. An additional size-effect can arise when $|\Delta G^c| \geqslant \Delta U_{se}$, resulting from changes associated with the inclusion–matrix interfacial energy. The question now is, which of these size effects is most critical and best explains the experimental observations.

Equations 18, 20 and 21 can be rearranged to express the normalized critical particles sizes for

(a) microcracking:

$$\frac{D_c^c}{D_{uc}} = \frac{1 + [\gamma_c g_c / (\gamma_m - g_s \gamma_t)]}{1 - (\Delta U_{se} f_c / |\Delta G^c|)}; \qquad (22)$$

(b) twinning:

$$\frac{D_c^T}{D_{uc}} = \frac{1 + [\gamma_T g_T / (\gamma_m - g_c \gamma_t)]}{1 - (\Delta U_{se} f_T / |\Delta G^c|)}; \qquad (23)$$

and

(c) microcracking plus twinning:

$$\frac{D_c^{c,T}}{D_{uc}} = \frac{1 + [(\gamma_c g_c + \gamma_T g_T) / (\gamma_m - g_c \gamma_t)]}{1 - (\Delta U_{se} f_c f_T / |\Delta G^c|)}, \qquad (24)$$

where D_{uc} is the critical particle-size for unconstrained powders, as defined by Equation 14. By making reasonable assumptions concerning the values of f_c, f_T and relative values for the surface energy terms, one can obtain a comparison between Equations 15, 22, 23 and 24 to judge the dominant size effect.

Recent results of Ito *et al.* [22] have shown that a single radial crack in its arrest position relieves approximately 10% of the strain-energy associated with the residual stress-field of a spherical inclusion. Thus, a value of $f_c = 0.9$ was chosen. Porter [23] has calculated that about 70% of the strain-energy for the constrained ZrO_2 transformation is associated with shear strain. Twinning is expected to relieve a large portion of the strain-energy and, thus a value of $f_T = 0.67$ was chosen, i.e., it was assumed that 33% of the strain energy can be relieved by twinning. With regard to the surface energy terms, it is reasonable to assume that the surface energy of the crack is greater than both the surface energy of the twin and the differential interfacial energy of the two states, i.e., $\gamma_c g_c > \gamma_T g_T \simeq (\gamma_m - g_s \gamma_t)$. Values chosen are:

$$\frac{\gamma_c g_c}{(\gamma_m - g_s \gamma_t)} = 10$$

and

$$\frac{\gamma_T g_c}{(\gamma_m - g_s \gamma_t)} = 1.$$

Substituting the values of these parameters into Equations 15 and 22 to 24, the normalized particle-size was plotted as a function of $\Delta U_{se}/|\Delta G^c|$, as shown in Fig. 3.

Fig. 3 maps the size requirements for retaining the tetragonal phase and indicates the type of strain-energy relieving phenomena (e.g., twinning, microcracking) that would be observed if these requirements are not met. Since ΔU_{se} is much less dependent on temperature and alloying composition relative to $|\Delta G^c|$, the axis of abscissas in Fig. 3 can either represent increasing temperature or increasing alloy composition.

It should be noted first that the normalized critical size for each phenomena tends to infinity at the temperature where $|\Delta G^c|$ equals the relieved strain energy. Also, the rate at which the critical size decreases with temperature is controlled by the numerator of each function. For a given ZrO_2 alloy, the first size-effect encountered during cooling (decreasing $\Delta U_{se}/|\Delta G^c|$) will be that due to both microcracking and twinning which, when combined, results in the largest decrease in strain energy. At a given temperature, where $|\Delta G^c| > \Delta U_{se} f_c f_T$, transformation will be accompanied by both microcracking and twinning when the normalized size of the transforming inclusion lies above the curve labelled "twinning + microcracking". With a further decrease in temperature, i.e., when $|\Delta G^c| > U_{se} f_T$, the size-effect for transformation and twinning arises. Normalized particle sizes that fall within the area bounded by the "twinning only" and "twinning + microcracking" curves will be transformed and twinned. Fig. 3 shows that the condition for transformation and microcracking (at temperatures where $\Delta G^c > \Delta U_{se} f_c$) is only of academic interest. This size requirement is less stringent than the previous two. The last size effect, due to the change in interfacial energy, which can only occur at temperatures where $|\Delta G^c| > \Delta U_{se}$, has a limited phase field in Fig. 3 between the curves marked "twinning only" (upper bound) and "no strain energy relief" (lower bound). This phase field indicates a limited inclusion size-range for transformation without twinning and microcracking.

Since each of the functions illustrated in Fig. 3 defines conditions where $\Delta G_{t \to m} = 0$, it is obvious that these functions define phase boundaries. Therefore, they can be used to construct a phase diagram to indicate the surface phenomena that will or will not accompany a transformation in normalized inclusion size against $\Delta U_{se}/|\Delta G_c|$ (e.g., temperature) space. As shown in Fig. 4, four phase fields are evident for the parameters used: (a) a tetragonal field, (b) a monoclinic + twinned +

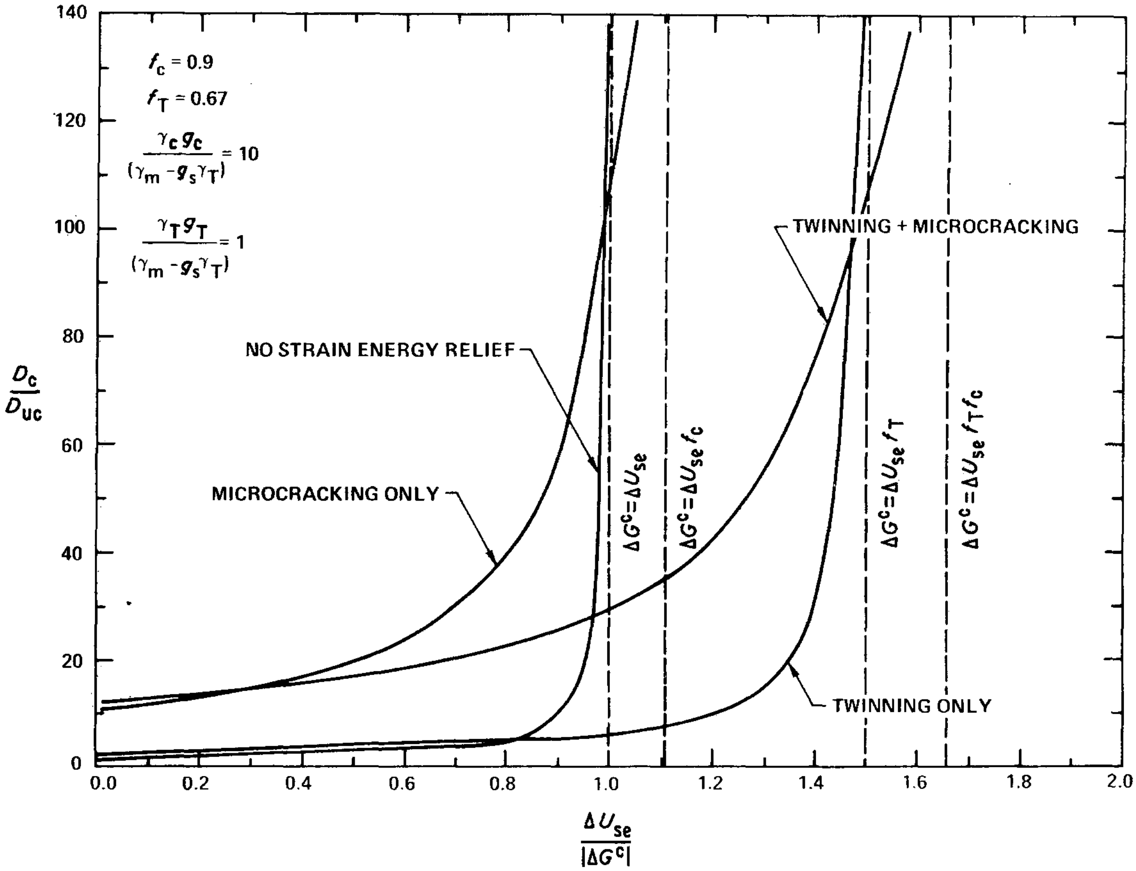

Figure 3 Plot of conditions where $\Delta G_{t\to m} = 0$ which includes various surface energy terms, as represented in normalized inclusion (grain) size against strain energy (ΔU_{se})/chemical free energy (ΔG^c) space.

microcracked field, (c) a monoclinic + twinned field and (d) a monoclinic field without twinning or microcracking. Unlike conventional phase diagrams, Fig. 4 includes the size of the inclusion that is introduced through the various surface energy terms. Although Fig. 4 is derived for specific parameters and would quantitatively change for other parameters, its general character (i.e., phase fields) will remain unchanged if $f_T > f_c$ and $\gamma_c g_c > \gamma_T g_T$.

The phase relations in Fig. 4 predict the following observations. If a composite with a wide distribution of inclusion sizes is cooled to a temperature where $\Delta U_{se}/|\Delta G^c| \simeq 1.2$, there will be a range of inclusions below a critical size still in their tetragonal state. Somewhat larger inclusions will be transformed and twinned, and still larger inclusions will be transformed, twinned and microcracked. If the same composite were only cooled to the temperature where $\Delta U_{sc}/|\Delta G^c| = 1.55$, inclusions larger than D_c would be transformed, twinned and microcracked and smaller inclusions would be untransformed. Composites with a very narrow size-distribution would be in only one of these phase fields. If appropriate experimental techniques were developed to independently observe twinning and microcracking, a composite with a wide inclusion size-distribution could be used to experimentally-determine the phase boundaries in Fig. 4.

Since the abscissa can also represent increasing alloy composition at a fixed temperature, Fig. 4 can be used to determine the effect of changing the alloy composition. For example, at a particular temperature and normalized inclusion size, an increase in alloy content would shift the transformation conditions from one phase field to another; an inclusion-size–composition phase diagram could be constructed at, for example, room temperature by heat-treating a number of different alloy compositions to increase the inclusion size, and then observing the inclusion size required for transformation, twinning and microcracking.

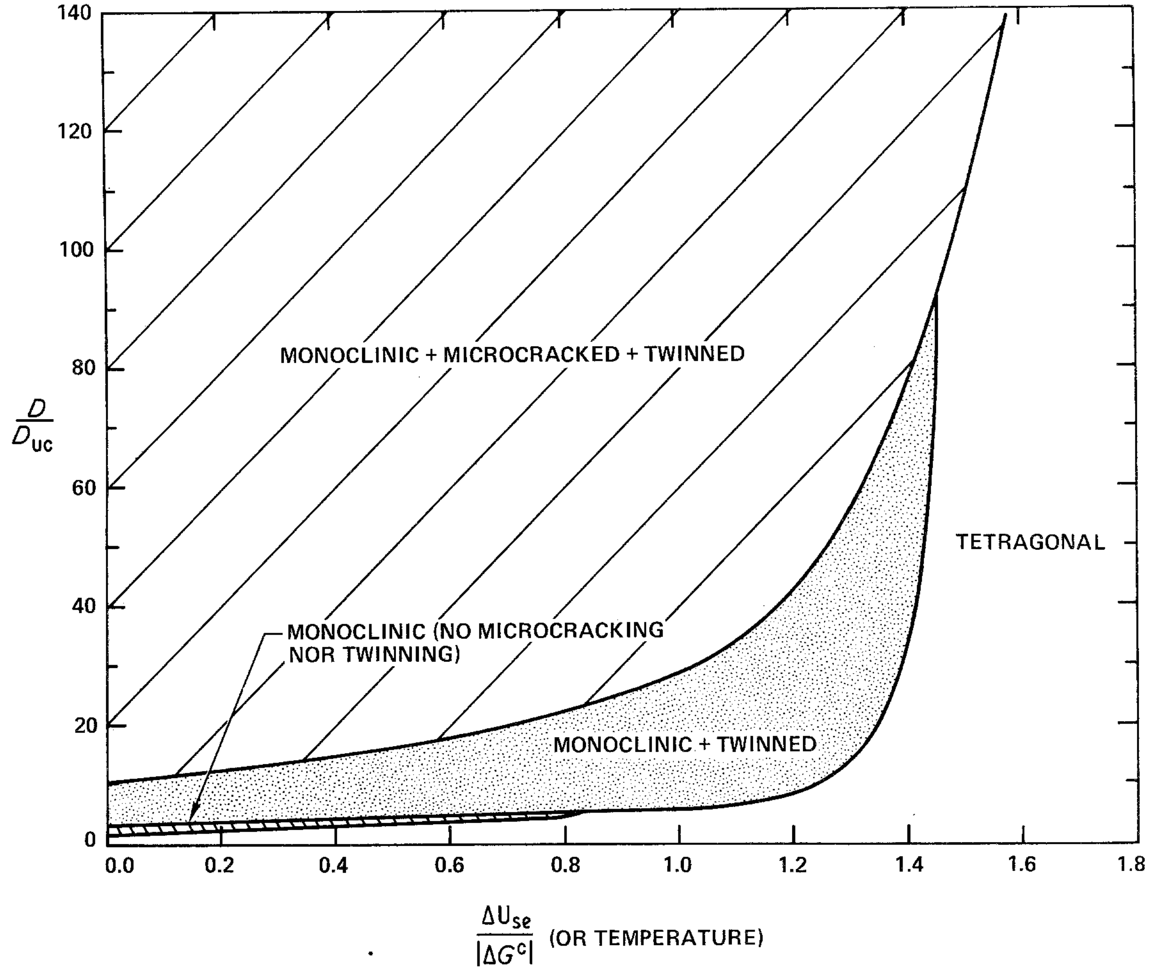

Figure 4 Phase regions defined by Fig. 3 indicating conditions of transformation and associated surface phenomena as a function of normalized particle size against temperature or alloy composition.

Without specific knowledge of the phase boundaries, it is obvious that the size effects discussed above are critical in fabricating a material in which the object is to retain the high-temperature phase upon cooling. If powder routes are used (i.e., sintering), powder sizes of less than D_c are required since grain growth during sintering is inevitable. If a solid-solution precipitation route is used, heat-treatment must be controlled to avoid precipitate growth of size greater than D_c. Thus, strict microstructural control is required in order that the high-temperature phase should be retained below its unconstrained transformation temperature.

On the other hand, the objective of fabrication may be to achieve the transformation but to avoid microcracking and/or twinning, as for the case of ferroelectrics. Ferroelectric materials are produced by constrained transformation. Twins (domains) form during the transformation, to primarily relieve strain energy (in non-conducting media, domains also reduce the external electric field due to polarization). Microcracking has also been observed to occur during transformations. Work on ferroelectric material cites several grain-size phenomena consistent with the arguments leading to Fig. 4. Matsuo and Sasaki [24] showed that when $PbTiO_3$ is fabricated with a grain size of about 10 μm, a high-microcracked body is produced upon cooling through its transformation temperature; however, a non-microcracked transformed material could be fabricated with a grain size of $\leqslant 3\,\mu$m. Buessem *et al.* [25] indicate that as the grain size of $BaTiO_3$ is reduced to about 1 μm, twinning is prevented during the transformation, which leads to a high permittivity. Thus, it can be seen that further work in defining the phase fields shown in Fig. 4 is of importance for a variety of useful constrained phase transformations.

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