

Thermodynamic analysis of the tetragonal to monoclinic transformation in a constrained zirconia microcrystal

Part 2 *In the presence of an applied stress*

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A thermodynamic analysis was made of a simple model comprising a transforming t-ZrO₂ microcrystal of size d constrained in a matrix subjected to a hydrostatic tensile stress field. The field generated a critical size range such that a t-particle transformed if $d_{cl} < d < d_{cu}$. The lower limit d_{cl} exists because at this point the maximum energy (supplied by the applied stress) which can be taken up by the crystal is insufficient to drive the transformation. The upper limit d_{cu} is a consequence of the microcrystal being so large that it transforms spontaneously when the material is cooled to room temperature. Using the thermodynamic (Griffith) approach and assuming that transformation toughening is due to the dilational strain energy, this mechanism accounted for about one-third of the total observed effective surface energy in a peak-aged Ca-PSZ alloy.

1. The critical size range for the transformation of a t-particle

In Part 1 of this series [1] a thermodynamic analysis was made of a constrained t-ZrO₂ particle transforming free of an applied stress. In the present work the analysis is extended to include the effect of an applied tensile stress on the constrained transformation. Such a study provides information on the maximum toughening effect to be expected for a given particle-matrix combination and also is useful in designing practical materials.

It is assumed that the applied stress is a hydrostatic tensile stress. That portion of the strain energy density generated by the applied stress which is involved in the thermodynamics of the transformation of a microcrystal is designated W_a , and is related to the interaction energy discussed by Eshelby [2]. To facilitate analysis, the particle is taken to be a spherical precipitate of t-ZrO₂ in Ca-PSZ or a spherical intergranular particle in an Al₂O₃-ZrO₂ alloy. The precipitate/particle is further assumed to be located within

the process zone near the crack tip; the process zone is defined as a region near the crack tip within which t-particles transform to m-symmetry due to the influence of the applied stress via the interaction energy term W_a . Fig. 1 illustrates the situation schematically. The thermodynamic description of the transformation is given by

$$\frac{\Delta F_0}{V} = \Delta F_{\text{chem}} + \Delta F_{\text{dil}} + \Delta F_{\text{shr}} + \frac{6\Sigma\Delta S}{d_c} + W_a < 0 \quad (1)$$

where ΔF_0 is the total change in free energy of the transformation, V is the volume of the microcrystal, ΔF_{chem} is the chemical (Helmholz) free energy, ΔF_{dil} is the strain energy density generated by the volume expansion associated with the t → m transforming, ΔF_{shr} is the residual shear stress after the microcrystal has twinned, $\Sigma\Delta S$ is the sum of all the interfacial energy terms and d_c is the critical diameter at

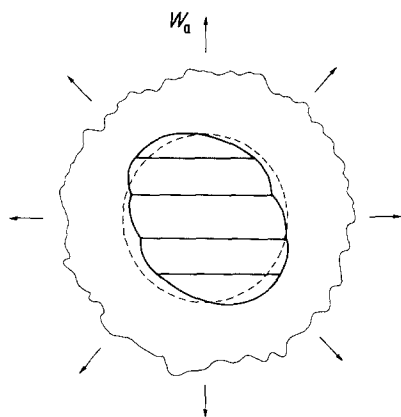


Figure 1 Schematic drawing of a constrained t-ZrO₂ particle transforming in the presence of an applied stress.

which transformation occurs for particular values of the temperature (M_s) and the applied stress. The various terms in Equation 1, except W_a , are discussed in detail elsewhere [1].

The effect of W_a is to allow more subcritical particles to transform at a particular M_s than would otherwise be the case. For example, at room temperature ($M_s \sim 300$ K), $d_c \sim 95$ nm for t-ZrO₂ precipitates in Ca-PSZ. Precipitates with $d < 95$ nm will not transform in the absence of an applied stress, because the term $6\sum\Delta S/d$ is too large and Equation 1 will be positive. If now a strain energy density W_a due to an applied stress is generated within the process zone, it will tend to nullify the dilational strain energy ΔF_{dil} , and allow initially subcritical particles to transform. Precipitates with a size $d < d_c$ will just transform when

$$-W_a = 6\sum\Delta S\left(\frac{1}{d} - \frac{1}{d_c}\right) \quad (2)$$

The maximum value that W_a can attain is

ΔF_{dil} , as far as Equation 1 is concerned; the applied stress cannot do more than compensate for ΔF_{dil} . This reasoning implies that there is a lower bound to the critical size d_{cl} , below which a particle cannot transform even if W_a exceeds ΔF_{dil} . This important point is now established that there is a critical size range for any given value of M_s within which t-particles can transform. The upper bound of the range d_{cu} occurs when the particles are large enough to transform spontaneously to m-symmetry when the material is cooled from the firing temperature to M_s . The lower bound d_{cl} exists because at this size there occurs the maximum value of the interaction energy which can be taken up by the microcrystal. To find the value of d_{cl} , set Equation 2 equal to ΔF_{dil} and solve for d .

The size dependence of W_a is plotted in Fig. 2 for Ca-PSZ and Al₂O₃-ZrO₂ materials at different values of M_s . Suitable values of ΔF_{dil} for both alloys have been discussed elsewhere [1]. The temperature dependence of the relationship between W_a and the critical size range was estimated by using Equation 1 in which ΔF_{chem} was given by $q(1 - T/T_b)$, where q is the heat of the transformation reaction, T is the transformation temperature (M_s) as a particle of a given size and T_b is the transformation temperature of an infinite crystal. The critical size range for Ca-PSZ at room temperature is 62 to 95 nm (Fig. 2a). The effect of increasing M_s is to broaden the critical range and shift it to higher values. The critical size range at room temperature for Al₂O₃-ZrO₂ materials is very narrow, amounting to only 0.38 to 0.45 μ m (Fig. 2b). This result suggests that transformation toughening in the bulk plays only a minor role in Al₂O₃-ZrO₂ alloys, as discussed

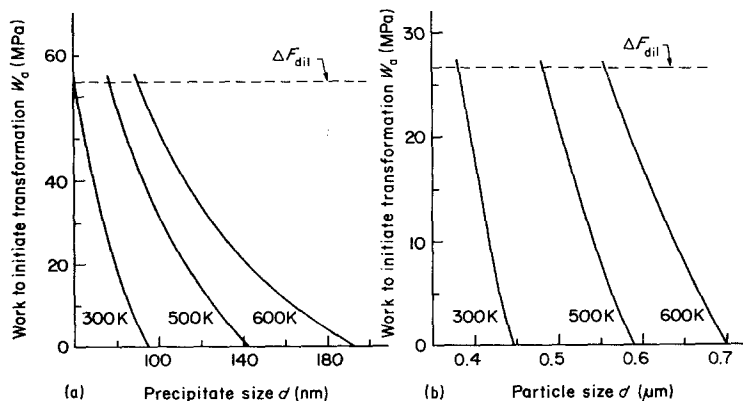


Figure 2 Size dependence of the interaction energy term W_a for (a) Ca-PSZ and (b) Al₂O₃-ZrO₂.

elsewhere [3, 4]. The effect of increasing M_s is similar to that observed for Ca-PSZ alloys. There is experimental evidence which lends some credence to the notion of a critical size range, as displayed in Fig. 2. Precipitates in Ca-PSZ near fracture surfaces never transform when the size is less than about 60 nm [5]. Recent studies on a commercial $\text{Al}_2\text{O}_3\text{-ZrO}_2$ alloy showed that the critical size range for the transformation of intergranular t -particles was only about $0.1 \mu\text{m}$ at room temperature [4]. These observations are in good agreement with the calculated values (Fig. 2).

2. Estimation of the toughening increment

The introduction of an applied stress into the thermodynamics of the transformation allows the possibility of estimating the toughening increment due to the $t \rightarrow m$ inversion in the process zone. This problem can be solved in two ways. The first is the Griffith thermodynamic approach in which the characteristic features of the process zone define an effective surface energy which adds on to the intrinsic surface energy of the composite (see Appendix). In the recent literature [6-8] this approach yields an equation of the form

$$K_T = \left[K_0^2 - 2ERV_f \left(\sum \Delta F_{\text{str}} + \Delta F_{\text{chem}} \right) \right]^{1/2} \quad (3)$$

where K_T is the fracture toughness of the composite, K_0 is the fracture toughness of the composite containing particles just too small to transform (i.e. $d \sim 60 \text{ nm}$ for Ca-PSZ). E is the Young's modulus and $\Sigma \Delta F_{\text{str}}$ is the total transformational strain energy ($\equiv \Delta F_{\text{dil}} + \Delta F_{\text{shr}}$).

As it is written Equation 3 is wrong. To find the correct equation, the following digression is necessary. The problem is that the term $(\Sigma \Delta F_{\text{str}} + \Delta F_{\text{chem}})$ is incorrect in principle as the proper thermodynamic quantity to define the toughening increment due to a transforming particle. The underlying thinking used in the literature to justify the selection of this term is that the toughening increment is due to energy W_a being absorbed in the process zone from the applied stress, which causes the particles to transform; that is, $-W_a = (\Sigma \Delta F_{\text{str}} + \Delta F_{\text{chem}})$. This reasoning is incorrect on two counts.

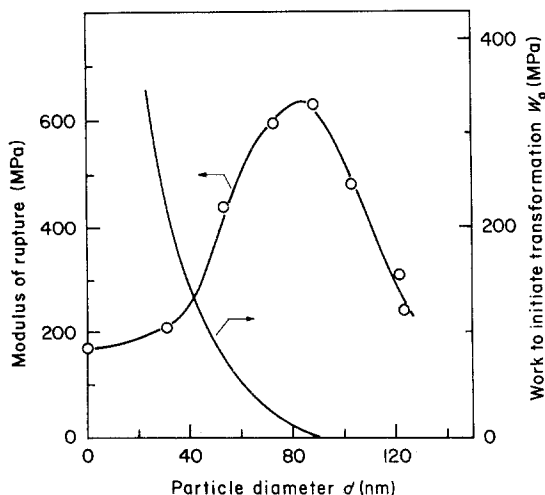


Figure 3 Size dependence of the interaction energy W_a and the strength of a Ca-PSZ alloy.

Firstly, the previous relationship can only be derived from Equation 1 on the assumption that the interfacial energy term $6\Sigma\Delta S/d$ is negligible. However, it is estimated that the contribution from this source amounts to about 23% of the total energy change for precipitates in a Ca-PSZ alloy [5]. Although the interfacial energies in themselves are small, it is the combination of the facts that the particle size appears in the denominator of the interfacial term and that the sizes involved are small which makes contributions from this source significant. More importantly, note that the term W_a is only invoked for sub-critical particles where size effects are significant. To discuss the former whilst simultaneously neglecting the latter is an exercise in illogic. The second error is the very concept that an energy W_a , supplied by the loading system and absorbed by transforming particles in the process zone, is responsible for the toughening increment. The fact is that in real materials the functional dependence of the toughness/strength on the interaction energy is opposite to that indicated by Equation 3. Consider Fig. 3 which is a plot of the precipitate size dependence of the strength (modulus of rupture, MOR) and the absolute value of the interaction energy W_a for a Ca-PSZ alloy [5]. Ground samples were used to obtain the strength data, so that values near the peak are too high by about 15 to 20% [9]. Values of the interaction energy were calculated from Equation 1 using data from the various terms which have been discussed elsewhere [1]. Note that where the maximum strength occurs the

precipitate size $\sim d_{cu} \sim 95$ nm, and only a small value of W_a is required to satisfy Equation 1 thereby allowing the transformation to occur. The minimum toughening effect occurs when the size $\sim d_{cl} \sim 62$ nm, where a large value of W_a is required to effect the transformation. Clearly the interaction energy term W_a cannot be used to estimate the toughening increment.

It is argued here that the correct energy term to estimate the toughening increment to a first approximation in Equation 3 is the dilational energy term ΔF_{dil} . Consider the case for mono-sized precipitates with $d \sim d_{cu}$ and $W_a \sim 0$. Before the transformation there is only a negligible strain energy density in the process zone. After the transformation the strain energy density is given by $\Sigma \Delta F_{str} = \Delta F_{dil} + \Delta F_{shr}$. On the assumption that the shear strain energy ΔF_{shr} does not interact with the applied stress, the loading system must supply an energy density equal, but opposite in sign, to ΔF_{dil} to restore the energy density within the zone to its original level. This assumption is reasonable because the experimental value of $d_{cl} \sim 60$ nm agrees with that calculated using $W_a = \Delta F_{dil}$ in Equation 2. The transforming particles do work on themselves and the surrounding matrix which must be overcome to restore the energy density to its original level. This is the source to transformation toughening and has been discussed by Hornbogen [10]. The energy density supplied externally which compensates for ΔF_{dil} is not the W_a which appears in Equation 1. This energy density is designated here the restoring energy density W_r .

Suppose now that the mono-sized precipitates have $d \sim d_{cl}$ and $W_a \sim \Delta F_{dil}$. Just prior to the transformation the strain energy density throughout the zone is ΔF_{dil} . During the transformation a strained t-particle with an energy density of about ΔF_{dil} becomes an m-particle with an energy density near to zero (neglecting ΔF_{shr}). Therefore, again, the loading system must supply an energy density $W_r = \Delta F_{dil}$ to restore the strain energy density in the zone to its original level. Although the transforming particle of size $\sim d_{cl}$ does no work on itself or its surroundings in the thermodynamic sense, it does relax the strain energy density which prevailed before transformation. At intermediate precipitate sizes, $d_{cl} < d < d_{cu}$, the effect of the transformation will be partly to relieve the

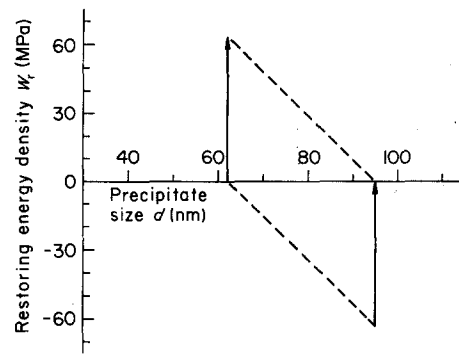


Figure 4 Size dependence of the restoring energy density W_r .

externally supplied energy W_a , and partly to do thermodynamic work on the particles themselves and their surroundings. Always, the loading system must supply an amount of energy $W_r = \Delta F_{dil}$ to restore the strain energy density in the zone to the level which existed before transformation occurred (neglecting ΔF_{shr}). Fig. 4 is a schematic illustration of the situation. According to this argument, the correct form of the equation which predicts the toughening increment, using the Griffith concept, is given (see Appendix) by

$$K_T = (K_0^2 + 2ERV_f W_r)^{1/2} \quad (4)$$

The second approach to predicting the toughening increment is one using fracture mechanics in which the crack tip is considered to be shielded from the applied stress by the process zone [11]. The fracture mechanics analysis yields the following equation:

$$K_T = K_0 + 0.22 EV_f \Delta V R^{1/2} \quad (5)$$

where ΔV is the transformational strain of a particle. To use Equations 4 and 5 requires knowledge of the particle size dependence of R and V_f . The size (and hence the K_T dependence) of V_f can be estimated on the assumption that any given mean precipitate size d is normally distributed with a standard deviation taken to be 16%. The latter figure was selected because it gave good agreement between calculated and experimental values of V_f . For a particular mean value of d , the fraction of transformable precipitates is the area under the normal curve for which $62 \text{ nm} < d < 95 \text{ nm}$. An example of this situation is shown in Fig. 5, where the fraction of transformable precipitates is found within the shaded region. The value of V_f is then half this

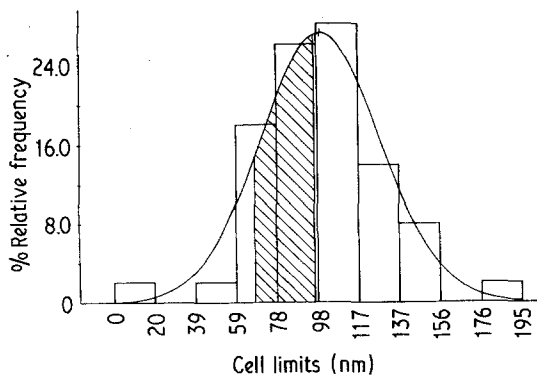


Figure 5 Particle size distribution of precipitates in a Ca-PSZ alloy.

amount, because the precipitate phase comprises about 50% of the Ca-PSZ alloy [12]. When the size distribution is cast in the standard form V_f is given by

$$V_f = \frac{1}{2} \frac{1}{(2\pi)^{1/2}} \int_{t(0)}^{t(u)} \exp(-t^2/2) dt \quad (6)$$

where $t(u) = (95 - d)/0.16d$ and $t(l) = (62 - d)/0.16d$. The size dependence of V_f is plotted in Fig. 6, where it is seen that this function is a controlling factor in the size dependence of the strength (Fig. 3).

In principle the size dependence of R can be calculated theoretically from Equation 2. For a given particle size $d < d_{cu}$ (at room temperature, say) the externally supplied strain energy density required in the process zone to effect the trans-

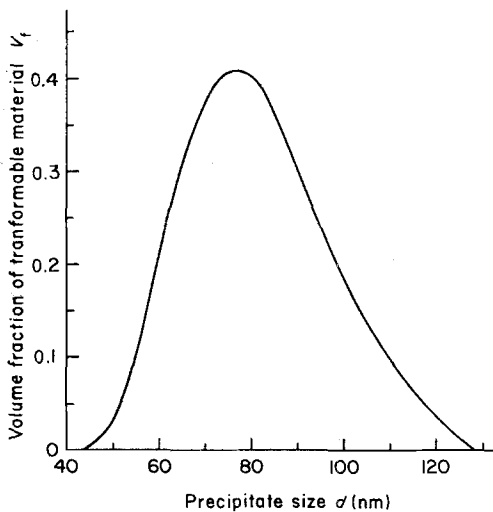


Figure 6 Size dependence of the volume fraction of transformable material V_f .

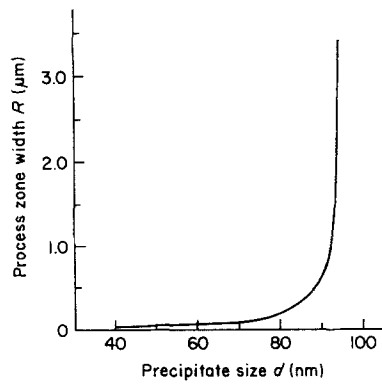


Figure 7 Theoretical size dependence of the process zone width R .

formation is given by

$$\frac{\sigma_a^2}{2E} = |W_a| = 6 \sum \Delta S \left(\frac{1}{d} - \frac{1}{d_{cu}} \right) \quad (7)$$

where σ_a is the applied stress. Taking advantage of the fact that prior to any transformation

$$\sigma_a = \frac{K_0}{(2\pi r)^{1/2}} \quad (8)$$

where r is the distance from the crack tip, and assuming that r is that distance at which precipitates of size d just transform so that $r = R$, then

$$\frac{1}{R} = \frac{24\pi E \sum \Delta S}{K_0^2} \left(\frac{1}{d} - \frac{1}{d_{cu}} \right) \quad (9)$$

The size dependence of R is plotted in Fig. 7, where it is seen that the zone size is unstable when $d \sim d_{cu}$. Mathematically, R becomes infinite in this region and physically the zone disappears because transformation occurs everywhere throughout the sample. The behaviour of real materials seems to bear some resemblance to that indicated by Fig. 7. Very large process zones with $R \sim 70 \mu\text{m}$ were observed in slightly overaged samples of Mg-PSZ (M. V. Swain, private communication). However, for underaged materials R -values predicted by Equation 9 are much less than those observed experimentally. Two factors could account for this discrepancy. First, real precipitates are characterized by a size distribution whereas Equation 7 is based on idealized mono-sized precipitates; thus precipitates larger than some nominal value of d will transform at values of $r > R$. Second, one transforming precipitate could "catalyse" the transformation of a

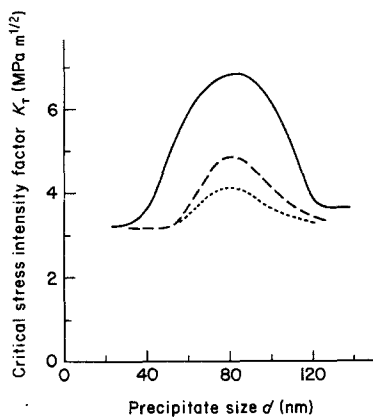


Figure 8 Comparison of calculated and experimental values of the fracture toughness of a Ca-PSZ alloy as a function of precipitate size.

neighbour. It is not straightforward to account for these effects analytically, so the size dependence of R was established empirically using data published elsewhere [13, 14].

Experimental values of K_T are plotted as a function of precipitate size in Fig. 8 (solid curve). These data were obtained by converting the strength values of Fig. 3 (corrected for surface compressive stresses) to K_T values, using published flaw size data [9]. Calculated values of K_T using the energy balance approach (Equation 4, dashed curve) underestimate the toughening increment ($K_T - K_0$) by about 53% at the peak value. The situation is worse using the stress field approach (Equation 5, dotted curve) with the underestimate increasing to about 74%. In principle both equations should yield similar results. The reason for the discrepancy is unknown.

Clearly transformation toughening is not the only toughening mechanism operating in the Ca-PSZ alloy. For example with a precipitate size of about 3 nm no t-precipitates transform, yet the K_T value is $3.2 \text{ MPa m}^{1/2}$ compared to the value of $1.7 \text{ MPa m}^{1/2}$ for the pure matrix phase, cubic stabilized zirconia (CSZ). Mechanisms which have been discussed in the recent literature include crack deflection and/or bowing [15] and microcracking [16]. Even if these contributions are included there will still be a large discrepancy between calculated and experimental values of the fracture toughness, as will be discussed below. When this fact is combined with the knowledge that both types of theoretical calcula-

tion give serious underestimates of the expected toughening increment, it suggests that there is an additional toughening mechanism which needs to be considered. A candidate for the unknown mechanism is plastic deformation, which has been observed operating in the precipitate-toughened alloys [17-19]. In the references cited the plastic deformation is associated with compressive stress fields. However, it has recently been observed that tensile stress-strain curves for Mg-PSZ alloys showed nonlinear behaviour which could be due to plastic deformation (M. V. Swain, private communication).

If it is assumed as a working hypothesis that plastic deformation contributes to the toughening increment, then a qualitative account can be given of the relative importance of the various mechanisms near the peak value using the following equation:

$$\Sigma K = [K^2(\text{CSZ}) + K^2(d/b) + K^2(\text{mc}) + K^2(\text{tt}) + K^2(\text{p})]^{1/2} \quad (10)$$

where the letters in brackets denote contributions to the total fracture toughness (ΣK) from CSZ free of any precipitates (CSZ), crack deflection/bowing from the precipitates as a dispersed second phase (d/b), microcracking from the larger t- and m- precipitates (mc), transformation toughening (tt) and plastic deformation (p), respectively. The formation of 30 nm t-precipitates in under-aged Ca-PSZ increases the fracture toughness to $3.2 \text{ MPa m}^{1/2}$ from $1.72 \text{ MPa m}^{1/2}$ measured for CSZ [9, 13]. The increase is likely to be due to crack deflection and/or bowing, which was observed to cause a similar increase in toughness in an m-ZrO₂/ZnO composite [15]. In the reference cited, t-ZrO₂ particles did not contribute to the toughness, unlike t-ZrO₂ precipitates in Ca-PSZ. The fact that under- and over-aged Ca-PSZ materials have similar strength suggests the possibility that the crack deflection/bowing contribution is approximately constant for precipitates in the range 30 to 120 nm. An estimate of this contribution can be made upon noting that

$$\begin{aligned} K_0 &= [K^2(\text{CSZ}) + K^2(d/b)]^{1/2} \\ &= 3.2 \text{ MPa m}^{1/2} \end{aligned} \quad (11)$$

whence $K(d/b) = 2.27 \text{ MPa m}^{1/2}$.

The toughness of over-aged Ca-PSZ ($3.7 \text{ MPa m}^{1/2}$) is somewhat larger than it is for

under-aged material ($3.2 \text{ MPa m}^{1/2}$). The increase could be due to crack deflection/bowing being more efficient for larger m-precipitates than for smaller t-precipitates. A second possibility is that large t- and m-precipitates cause microcracking as has been observed elsewhere [16]. Assuming that the latter situation prevails, the microcracking contribution to toughness is given by

$$\begin{aligned} & [K^2(\text{CSZ}) + K^2(d/b) + K^2(\text{mc})]^{1/2} \\ & = 3.7 \text{ MPa m}^{1/2} \end{aligned} \quad (12)$$

so that $K(\text{mc}) \sim 1.9 \text{ MPa m}^{1/2}$. The contribution due to transformation toughening $K(\text{tt})$ is calculated to be about $3.8 \text{ MPa m}^{1/2}$ assuming, arbitrarily, that the thermodynamic approach (Equation 4) gives the correct result. When the previous toughness values from the various sources are inserted into Equation 10, the contribution from the proposed plastic deformation, $K(\text{p})$, amounts to $4.2 \text{ MPa m}^{1/2}$.

To obtain some idea of the relative importance of the various mechanisms the toughness values must be converted to fracture energies (Γ), using the relation

$$\Gamma = \frac{K^2}{2E} \quad (13)$$

Taking advantage of the fact that fracture energies are additive, and noting that E has a constant value of about 207 GPa throughout the ageing sequence, one obtains [9, 20]

$$\begin{aligned} \sum \Gamma &= \Gamma(\text{CSZ}) + \Gamma(d/b) + \Gamma(\text{mc}) \\ &+ \Gamma(\text{tt}) + \Gamma(\text{p}) \end{aligned} \quad (14)$$

$$\begin{aligned} 112 \text{ J m}^{-2} &= 7.1 (6\%) + 17.6 (16\%) \\ &+ 8.7 (8\%) + 34.9 (31\%) \\ &+ 42.6 (38\%) \end{aligned}$$

Transformation toughening and the proposed plastic deformation mechanism are the two most important toughening mechanisms, comprising 31% and 38% respectively of the total effective surface energy of the peak-aged alloy.

3. Conclusions

(a) The effect of an applied stress on the thermodynamics of the transformation in a constrained t-ZrO₂ microcrystal is to generate a critical size range within which the particles transform.

(b) The proper energy term to calculate the

toughening increment due to transformation toughening in the energy balance approach is the dilatational strain energy, which is independent of the applied stress, and approximately independent of particle size.

(c) Transformation toughening accounts for about one-third of the total observed effective surface energy of a peak-aged Ca-PSZ alloy.

Appendix

The toughening increment using the thermodynamic approach

The reduction in strain energy U of a tensile, elastic plate of unit width containing a crack of length $2C$, subjected to an applied stress σ_a , is [21, 22]

$$U = \Pi^2 C \sigma_a^2 / e \quad (A1)$$

where E refers to plane stress. The reduction in strain energy is opposed by the energy required to create the crack surfaces, namely

$$U_s = 4C\Gamma_0 \quad (A2)$$

The condition for crack propagation is found by equating the total change in energy per incremental increase in crack length to zero. The situation is complicated by the presence of a process zone. The dilatational strain energy due to the t \rightarrow m transformation reduces the tensile strain energy in the zone; to supply strain energy to the crack tip at the same rate, the applied stress must restore the strain energy in the zone to the original level which existed before transformation occurred. The transformational strain energy can therefore be regarded as an increase in the effective surface energy. The transformational strain energy U_{tsc} is a product of the volume of the process zone, the fraction of the material which transforms and the dilatation strain energy density ΔF_{dil} . The volume of the process zone is approximately that of two parallelepipeds of unit width, each adjacent to a crack surface and of cross-section $(2R + 2C)R$, so that

$$U_{\text{tsc}} = 4RCV_f \Delta F_{\text{dil}} \quad (A3)$$

where $R \ll C$. Applying the condition for crack propagation,

$$\begin{aligned} \frac{\Delta \sum U}{\Delta C} &= -2\pi C \sigma_a^2 / E + 4\Gamma_0 + 4RV_f \Delta F_{\text{dil}} \\ &= 0 \end{aligned} \quad (A4)$$

or

$$K_T = (K_0^2 + 2ERV_f \Delta F_{\text{dil}})^{1/2} \quad (A5)$$

Other attempts to use the thermodynamic approach have been made in the recent literature which require comment, because they are in error [6–8]. Evans and Heuer [6] derived the following equation:

$$\Gamma_t = \Gamma_0 + 2Rf(\Delta U_T - V_p \Delta G_0) \quad (\text{A6})$$

where Γ is the surface energy, f is the number of particles per unit volume, ΔU_T is the total transformational strain energy of a single particle, V_p is the particle volume and ΔG_0 is the change in chemical free energy per mole of the transformation. Expressing Equation A6 in terms of the fracture toughness one obtains

$$K_T = [K_0^2 + 4ERf(\Delta U_T - V_p \Delta G_0)]^{1/2} \quad (\text{A7})$$

The wrong choice of energy term to calculate the toughening increment has been discussed in the main text. Other difficulties with Equation A7 are that the units in the second term on the right-hand side are dimensionally incorrect, and the numerical factors should be two rather than four. The reason for the latter discrepancy is that Evans and Heuer write that the change in effective surface energy with respect to an incremental increase in crack length is $2\Gamma_0$, in the absence of any transformation. However, the standard result for this quantity for the case of an interior slit crack of length $2C$ is $4\Gamma_0$, as in Equation A2 [21, 22].

According to Claussen and Rühle [7], the toughening increment due to a process zone using the thermodynamic approach is

$$K_T = [K_0 + 2ERV_f(\Delta U_T + \Delta G_{\text{chem}})]^{1/2} \quad (\text{A8})$$

Apart from the wrong choice of energy terms the major flaw with this result is that it is based on the idea that the fracture toughness increments from various sources are additive, whereas the accepted concept is that it is the various contributions to the effective surface energy which are additive [20]. Therefore the squares of the various fracture toughness increments must be added if the thermodynamic approach is used. Using the energy balance concept, Lange [8] derived the following equation:

$$K_T = \left[K_0^2 + \frac{2ERV_f(\Delta G - \Delta U_T F)}{(1 - \nu^2)} \right]^{1/2} \quad (\text{A9})$$

where $(1 - F)$ is the loss of strain energy due to

any microcracking and ν is Poisson's ratio. The same comments concerning the energy term that were made previously apply also to Equation A9.

When the confusion as to the correct choice of the energy term and its sign are clarified according to the view presented in this work, then Equations A7 to A9 are equivalent to Equation A5.

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