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Thermodynamics of the tetragonal to monoclinic phase transformation in constrained zirconia microcrystals

Part 1 *In the absence of an applied stress field*

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End-point thermodynamic analyses were made of the tetragonal to monoclinic transformation (t → m) occurring in ZrO_2 precipitates in a Ca–PSZ alloy and particles in Al_2O_3–ZrO_2 composites. Calculated plots of the reciprocal critical size for transformation temperature were in excellent agreement with experimental data for both systems. Contributions to the total free energy change included bulk chemical, dilatational and residual shear strain energies and also interfacial energies. The latter term consisted of contributions from the change in the chemical surface free energy, the presence of twin boundaries in the precipitate (particle)–matrix interfacial energy. The major impediment to the transformation was the shear strain energy which could not be reduced sufficiently by twinning alone. The t → m reaction proceeded spontaneously when the energy barrier was reduced by the response of the particle–matrix interface. The response comprised loss of coherency and grain boundary microcracking for the Ca–PSZ and Al_2O_3–ZrO_2 alloys, respectively. These results are in accord with recent suggestions that either a stress-free strain or a free surface is a necessary conditions for the initiation of a martensitic transformation.

1. Introduction

Hannink *et al.* showed experimentally that the reciprocal critical size of precipitates for the t → m transformation in a Ca–PSZ alloy was a linear function of the transformation temperature [1]. A thermodynamic analysis of the transformation, presented in that work, showed that such a relationship could be expected theoretically if the total free energy change of the inversion included bulk and interfacial energy terms. The slope and intercept of the experimental plot yielded values for the strain and interfacial energies which were considerably larger than the expected values. The reason is that Hannink *et al.* considered only bulk chemical and dilatational strain energy contributions plus changes in the chemical surface free energy and precipitate–matrix interfacial energy (loss of coherency). Lange and Evans *et al.* also extended the thermodynamic approach to include a bulk residual shear strain energy contribution from the twinning process, interfacial contributions from twin boundaries and microcracking at the particle–matrix interface where appropriate [2, 3]. Claussen and Rühle and also Heuer *et al.* recently have obtained data on the temperature dependence of the critical particle size for transformation in Al_2O_3–ZrO_2 composites [4, 5]. It is therefore appropriate to attempt more refined end-point calculations which include these data and the additional bulk and interfacial energy terms discussed above.

Heuer *et al.* have suggested that nucleation plays a key role in the particle size–transformation temperature (M_s) relationship observed in the transformation of tetragonal grains or precipitates. However, despite years of extensive study and

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TABLE I Definition of the initial and final states of the transformation

Ca–PSZ		Al_2O_3–ZrO_2	
Initial	Final	Initial	Final
Tetragonal	Monoclinic	Tetragonal	Monoclinic
Coherent	Incoherent	Incoherent	Incoherent
Single crystal	Twinned	Single crystal	Twinned
	Expanded		Microcracked
			Expanded

numerous attempts (see Olson and Cohen [6] for a recent review), such an approach has not yielded a quantitative basis for the application of such a model. In contrast, the readily transparent "end-point" thermodynamic approach, as outlined below, does provide a quantitative basis for the prediction of the critical particle size at a particular value of M_s.

Two different systems containing ZrO_2 precipitates and particles will be considered, namely Ca–PSZ and Al_2O_3–ZrO_2, the latter containing intergranular particles. The initial and final states of the microcrystals in these systems are defined in Table I.

The free energy description of the transformation occurring in a spherical, constrained microcrystal of radius, r, has the following form, in the absence of an applied stress:

$$\Delta F_0 = \tfrac{4}{3}\pi r^3(\Delta F_{\text{chem}} + \Delta F_{\text{dil}} + \Delta F_{\text{shr}}) + 4\pi r^2(\Delta S_{\text{chem}} + \Delta S_{\text{tw}} + \Delta S_{\text{p/m}}), \quad (1)$$

where ΔF_0 is the total free energy change, ΔF is the free energy change per unit volume, the subscripts chem, dil and shr referring to chemical, dilatational and shear energy contributions, respectively. Free energy changes per unit area are denoted by ΔS and the subscripts tw, p/m refer to contributions from the twin boundaries and the precipitate (particle)/matrix respectively.

Equation 1 can be written more conveniently as:

$$\frac{\Delta F_0}{V} = \Delta F_{\text{chem}} + \Sigma\Delta F_{\text{str}} + \frac{3}{r}\Sigma\Delta S, \quad (2)$$

where V is the volume of the microcrystal, $\Sigma\Delta F_{\text{str}}$ is the sum of the strain energies and $\Sigma\Delta S$ is the sum of the interfacial energy contributions. Upon applying the condition for equilibrium and expressing ΔF_{chem} in terms of experimental variables, Equation 2 becomes:

$$\frac{1}{r_c} = \frac{q}{3\Sigma\Delta S T_b}\,T - \frac{q + \Sigma\Delta F_{\text{str}}}{3\Sigma\Delta S}, \quad (3)$$

where the subscript, c, denotes a critical value, q is the enthalpy of the transformation of an infinitely large crystal and T is the transformation temperature (M_s) of a microcrystal of radius r_c. Equation 3 shows the origin of the linear relationship observed between r_c^{-1} and T.

2. Calculations

2.1. Ca–PSZ

The chemical free energy change, ΔF_{chem} is given by $q(1 - T/T_b)$ for both materials and becomes $-285 \times 10^6(1 - T/1448)$ J m^{-3} (MPa) upon inserting the appropriate numerical values [7]. The dilatational strain energy is given by:

$$\Delta F_{\text{dil}} = \frac{k}{6}(\Delta V/V)^2 \quad (4)$$

where k is derived from the precipitate (particle and matrix elastic constants and $\Delta V/V$ is the fractional volume change associated with the t → m transformation. The elastic constant, k is calculated from the expression

$$k = \frac{2E_m E_p}{(1 + \nu_m)E_p + 2(1 - 2\nu_p)E_m}, \quad (5)$$

where E is Young's modulus and ν, Poisson's ratio. The subscripts m, p refer to matrix and precipitate (particle), respectively. For Ca–PSZ it is reasonable to assume that $E_m = E_p = 207$ GPa and $\nu_m = \nu_p = 0.25$ [8]. The fractional volume change associated with the transformation was calculated to be 0.0455 from the data of Hannink *et al.* obtained from precipitates [1]. Insertion of these values into Equations 4 and 5 yields a value of 63.5 MPa for ΔF_{dil}. The pure shear strain energy is given by

$$\Delta F_{\text{shr}} = \tfrac{1}{2}\mu\gamma^2 \quad (6a)$$

$$= \tfrac{1}{2}\tau\gamma \quad (6b)$$

where μ is the shear modulus, γ the shear strain and τ is the shear stress. The shear modulus was estimated to be $0.4E$, using the relation $\mu = E/2(1 + \nu)$. The shear strain was taken to be tan 8.9° [1]. From Equations 6a and b the shear strain energy and the shear stress amount to 1.0 GPa and 13.0 GPa, respectively. Clearly the shear strain energy is the major barrier to the transformation, which cannot proceed unless the microcrystal finds some means of reducing it to a level which will satisfy Equation 3. The shear strain will be reduced significantly if the precipitate loses

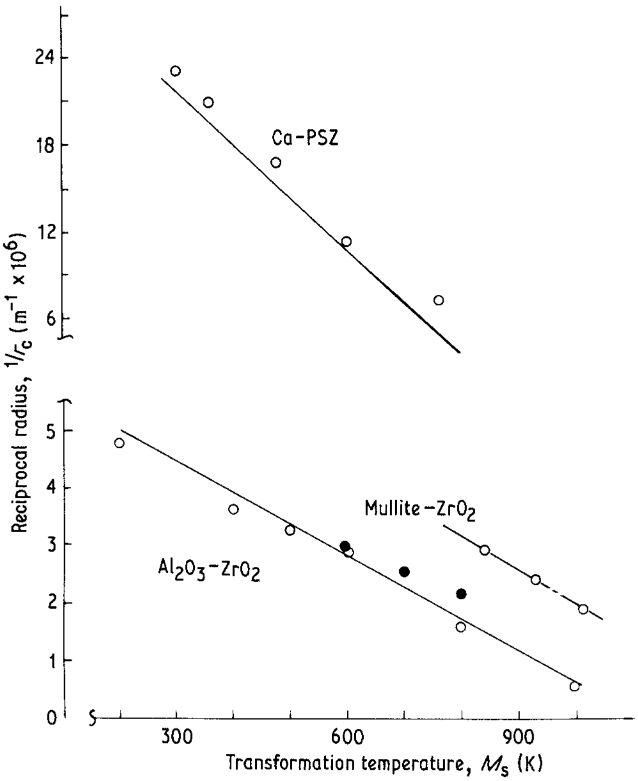

Figure 1 Temperature dependence of the reciprocal critical radius for the t → m transformation in Ca–PSZ, Al_2O_3–ZrO_2 and mullite–ZrO_2 materials.

coherency at the moment of transformation. When this occurs, the shear stress associated with the transformation is reduced to the yield stress, ~7.2 GPa. The latter quantity was estimated using the procedure of Marsh [9]. Using Equation 6b, ΔF_{shr} is reduced to 563 MPa. There will be a further reduction in shear strain energy due to the twinning process. This can be calculated using the following equation developed by Evans *et al.* [3]:

$$\Delta F_{\text{shr}} = \frac{1}{2}\tau\gamma \, \frac{0.64}{\eta} \qquad (7)$$

where η is the number of twins. The latter quantity was assumed to be 8 because it gave an estimate of 45.0 MPa for ΔF_{shr} close to the "experimental" value of 47.5 MPa. The latter quantity is the difference between the total experimental value of the strain obtained from the plot of r_c^{-1} against T ($\Sigma\Delta F_{\text{str}} = 111$ MPa) and the value of ΔF_{dil} calculated above. Eight twins is a reasonable number frequently observed in transformed precipitates in Ca–PSZ (R. H. J. Hannink, private communication).

The fact that the t → m transformation is associated with the evolution of heat guarantees that the surface energy of the monoclinic phase is greater than when the crystal has tetragonal symmetry. This point has been argued in detail elsewhere [7]. The expected increase in ΔS_{chem} was observed to be ~0.36 J m^{-2} [10]. Initially, we suppose that the t-precipitates are coherent but after transformation they are incoherent [11]. This change in the interfacial energy, $\Delta S_{\text{p/m}}$, was estimated to be 0.88 J m^{-2} [7]. Evans *et al.* estimated the contribution from the twin boundaries, using the following equation [3]:

$$\Delta S_{\text{tw}} = \frac{(\eta - 1)(\eta + 1)}{6\eta} \times \Gamma_{\text{tw}} \qquad (8)$$

where Γ_{tw} is the energy of a twin boundary. To obtain the best fit with the experimental data Γ_{tw} is taken to be 0.43 J m^{-2}, which is an acceptable value [7].

The calculated bulk and interfacial energy terms inserted into Equation 3 give the following relationship between the reciprocal critical radius and the transformation temperature:

$$\frac{1}{r_c} = (-3.65 \times 10^4 T) + (3.27 \times 10^7). \qquad (9)$$

Equation 9 is plotted in Fig. 1, together with experimental data, with excellent agreement [11].

2.2. Al_2O_3–ZrO_2

The bulk chemical free energy, ΔF_{chem}, for a transforming particle remains the same in this system as in Ca–PSZ materials. The calculation of the dilatational strain energy needs to be modified in two ways. First, it is assumed that microcracking is concurrent with the t → m transformation at temperatures below ~900° C because of the evidence presented by Green and Claussen *et al.* [12, 13]. This means that the value of E_m is reduced from 400 to ~374 GPa. Details of this calculation have been given elsewhere [12]. The second modification is an effective reduction in the volume expansion of the transformation of ~2% because the thermal expansion of alumina ($\alpha_a = 7.3 \times 10^{-6}\ {}^\circ C^{-1}$, $\alpha_c = 8.6 \times 10^{-6}\ {}^\circ C^{-1}$ in the range 27 to 1100° C) is less than that of t-ZrO_2 ($\alpha_a = 13.3 \times 10^{-6}\ {}^\circ C^{-1}$, $\alpha_c = 15.2 \times 10^{-6}\ {}^\circ C^{-1}$) [14, 15]. The new value for $\Delta V/V$ is 0.0255. The value of ΔF_{dil} for the composite using Equations 4 and 5 is 26.6 MPa.

Using Equations 6a and b the pure shear strain energy density and shear stress amount to 2.0 and 25.1 GPa respectively, for this composite. Again the shear strain energy density constitutes the major impediment to the transformation. The yield stress at room temperature was calculated to be 13.8 GPa using Marsh's procedure [9]. From Equation 6b, ΔF_{shr} amounts to 1.1 GPa, which is still too large to allow the transformation to occur even at cryogenic temperatures. Such a high value of the yield stress supports the view that microcracking must be concurrent with the transformation in the bulk in these composites, provided the particle separation is such that the transformation strains of one particle do not affect its neighbour.

How is the microcrack initiated? At room temperature the critical size for spontaneous microcracking due either to thermal expansion mismatch alone or to the net volume expansion of the particle after transformation is respectively 3 and 2 orders of magnitude greater than the critical size for spontaneous transformation at room temperature [16]; we conclude that this is not a likely source for the initiation of microcracks. Instead we suggest that the incipient shear stress of the metastable transforming intergranular microcrystal causes a pile-up of dislocations at the particle–matrix interface, thereby initiating a radial microcrack in the grain boundary. Such a mechanism can reduce markedly the shear strain energy associated with the transformation, as follows. According to Davidge, the stress required to nucleate a microcrack by this means is given by [17]:

$$\sigma_{\text{gb}} = \sigma_0 + \left[\frac{20E\Gamma_{\text{gb}}}{(1+\nu)d}\right]^{\frac{1}{2}} \tag{10}$$

where σ_{gb} is the grain boundary fracture stress, σ_0 is the Peierls stress (negligible in this case), Γ_{gb} the grain boundary fracture energy, and d is the ZrO_2 particle diameter. The value selected for Γ_{gb} is 2.8 J m^{-2} because it has been shown that $\Gamma_{\text{gb}} = 0.48\ \Gamma_{\text{cl}}$ where the latter symbol is the cleavage energy of sapphire ~6.0 J m^{-2} [18, 19]. Inserting this value into Equation 10 together with the other known quantities of 400 GPa, 0.2 and 0.5 μm for E, ν and d, respectively gives a value of $\sigma_{\text{gb}} \sim 4.5$ GPa. It is suggested that this value should be used for τ in Equation 6b so that ΔF_{shr} now comes to ~352 MPa. As before, there is a further reduction in ΔF_{shr} due to the twinning process in accord with Equation 7 to give a final value of 37.6 MPa where the number of twins, η, is assumed to be 6. We justify selecting this value because it is in the mid-range of the twin numbers observed and also gives the reasonable agreement with the value of ΔF_{shr} expected from the plot of r_c^{-1} against M_s shown in Fig. 1.

There will be the same increase for the chemical surface free energy, ΔS_{chem} (= 0.36 J m^{-2}) as before. There will be no contribution to the interfacial energy from a loss of coherency as the particles are incoherent both before and after the transformation. Instead, there will be a contribution from microcracking based on a geometry comprised of a lenticular radial crack in the grain boundary with the particle at its centre. The extension of the microcrack from the periphery of the particle into the grain boundary is one particle diameter [12]. The energy associated with microcrack formation is given by:

$$\Delta S^*_{\text{p/m}} = 2[\pi(3r)^2 - \pi r^2]\Gamma_{\text{gb}}. \tag{11}$$

To use Equation 11 in conjunction with Equations 1 and 3 it is convenient to write:

$$\Delta S = 4\Gamma_{\text{gb}} = 11.2\ \text{J m}^{-2}, \tag{12}$$

where $\Delta S_{\text{p/m}} = \Delta S^*_{\text{p/m}}/4\pi r^2$. The contribution from the twin boundaries, ΔS_{tw} is estimated to be 0.42 J m^{-2} from Equation 8. The calculated bulk and interfacial energy terms are again inserted into Equation 3 to give the following relationship:

$$\frac{1}{r_c} = (-5.48 \times 10^3 T) + (6.14 \times 10^6). \tag{13}$$

Equation 13 is plotted in Fig. 1 along with the experimental data for two alumina–zirconia alloys [4, 5]. Again there is good agreement between the data and the calculated line.

Recently, limited r_c against M_s data were published for a mullite–zirconia composite containing intergranular particles [20]. These data are also plotted in Fig. 1. The slope of the plot is similar to that for the Al_2O_3–ZrO_2 data, indicating that similar interfacial energies are involved for both composites. This is a reasonable conclusion if microcracking is concurrent with transformation also in the mullite–ZrO_2 material. The intercept of the plot for the latter composite is greater than that of the Al_2O_3–ZrO_2 ceramic, which is consistent with the fact that the thermal expansion of mullite is smaller than that for alumina. The low thermal expansion coefficient of mullite ($\alpha = 5.6 \times 10^{-6}$ $^\circ C^{-1}$ in the range 25 to 1500° C [21]) implies a reduced transformation toughening effect in the composite. Indeed, the total strain energy estimated from the plot in Fig. 1 is only 14.5 MPa, which necessarily includes a shear strain component. This analysis suggests that the reported increase in strength of an *in situ* composite compared to pure mullite is a consequence of some effect other than transformation toughening [20]. It was suggested that ZrO_2 particles altered the interfacial energies of amorphous material in the grain boundaries. Possibly this resulted in stronger grain boundaries and hence, a stronger composite. A similar effect was observed when Y_2O_3 or CeO_2 was added to Si_3N_4 composites [22].

3. Discussion

Our view is that a constrained t-ZrO_2 microcrystal cannot transform until M_s is reduced sufficiently to satisfy Equation 3. Usually such end-point calculations cannot shed light on the nature of the transformation. However, it seems that in this case the end-point calculations themselves imply something about the mechanism of the inversion. For example an energy barrier to nucleation only exists in Ca–PSZ in the absence of a dislocation at the precipitate–matrix interface and in Al_2O_3–ZrO_2, the absence of a microcrack at the particle–matrix boundary (Fig. 2). Once these interfacial disturbances exist there is little or no barrier to the nucleation and growth of the m-phase. If this view is correct, it must be very difficult to distinguish between the nucleation and growth stages of the transformation. A possible objection to the calculations presented in this work is the fact that a t-ZrO_2 particle does not know that it is going to twin at the onset of the transformation, therefore a large shear strain energy density barrier to transformation should exist until twins are formed. However, if the nuclei and initial product exist as thin plates then the shear strain energy density will be reduced to an acceptable level (such that $\Delta F_0 = 0$) by the ratio of the plate thickness to its diameter. In addition, if the transformation proceeds via a soft phonon mode mechanism to be discussed later, then the mere presence of a free surface or dislocation spontaneously lowers the free energy for transformation. The thermodynamic analysis, so far, has been concerned only with the t- and m-states labelled in Fig. 2. In principle there is no conflict between end-point calculations and mechanisms of nucleation because the latter must be contained within the former; nuclei formation and growth to the critical size are transient phenomena which exist between the initial and final states of the system.

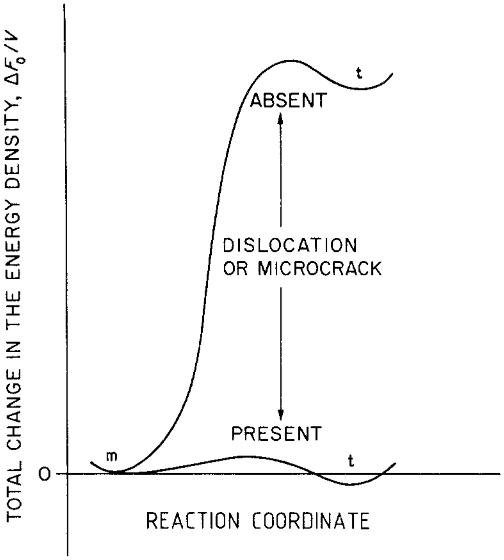

Figure 2 Schematic diagram of the energy barrier for the t → m transformation of a constrained microcrystal.

A different view of the lowering of M_s has been offered by other authors which is in conflict with the analysis presented here because they tend to neglect interfacial energy contributions to the total energy change [5, 23, 24]. Under this condition, Equation 2 is always negative but the ZrO_2 microcrystals, supposedly, are prevented from transforming as they should by an energy barrier. Nuclei of the m-phase formed from pre-existing embryos located at the particle–matrix interface are enabled to overcome the barrier by non-hydrostatic stresses generated by the mismatch in thermal expansion between the inclusion and host phase [5]. These stresses are amplified at sharp facets of the microcrystals, the degree of amplification being dependent on the particle size. In this way, the model takes account of the particle size effect illustrated in Fig. 1.

Experimental evidence is cited to support this model, as follows. The critical diameter, d_c, at room temperature for rounded intra-granular t-ZrO_2 particles in an alumina matrix is greater than it is for faceted inter-granular ZrO_2 particles. Also, d_c has a range of values for a given temperature for intra-granular particles but is single-valued for inter-granular particles. The suggestion is that rounded intra-granular particles do not amplify the non-hydrostatic stresses effectively so that nucleation of these particles is more difficult and no sharp M_s temperature can be observed. In addition, Heuer *et al.* observed that the M_s temperature of intra-granular particles was lowered after an 8 vol% ZrO_2–Al_2O_3 composite was annealed at 1500° C for 33 h although there was no discernible change in the particle morphology or size distribution [5]. This effect was attributed to the removal of the most active embryos by annealing. Thus a further reduction in M_s is required to activate the remaining less efficient embryos.

The present authors believe that the phenomena discussed in the previous paragraph can be interpreted more naturally in a manner which is consistent with the end-point analysis. Transforming intra-granular particles generate microcracks involving the higher cleavage fracture energy ($\sim 6\,J\,m^{-2}$) rather than the grain boundary fracture energy ($\sim 3\,J\,m^{-2}$). This has the effect of increasing the value of d_c at room temperature to $\sim 0.9\,\mu m$, consistent with the data of the pertinent reference [5]. The range of values for d_c observed for intra-granular particles is probably due to the fact these particles seem to form in close-packed clusters in which the particle separation is less than d_c; in fact, many of the intra-granular particles are touching as seen in Fig. 2 of the cited reference [5]. This situation introduces an autocatalytic feature into the transformation because the stresses from one transforming particle of the critical size can induce the inversion in a neighbouring, sub-critical particle and so produce a range of values for d_c, as observed. Also, if the particle separation is less than d_c, the length of the radial microcrack emanating from the particle–matrix interface could vary, which would influence the value of d_c. By way of contrast the particle separation of the inter-granular particles (Fig. 3, ref [5]) tends to be larger than d_c so that the transformational stresses of one particle has less influence on a neighbour, resulting in a unique value for d_c.

We agree that the reduction of M_s by prolonged annealing at 1500° C observed by Heuer *et al.* [5] is probably the result of removal of embryos. We suggest that the thermodynamic analysis allows us to specify that these embryos are in fact microcrack nuclei which are healed (annealed out) in the manner observed by Green [12]. Claussen *et al.* [13] noted that the *E*-modulus of an Al_2O_3–ZrO_2 composite containing super-critical ZrO_2 particle was time dependent when it was cooled to room temperature after being heated to 1275° C; the *E*-modulus decayed exponentially to a stable value of 282 MPa from an initial value of 328 MPa after 12 h. This phenomenon was attributed to slow microcrack growth caused by the transforming ZrO_2 particles. This suggests that the M_s temperature of the 8 vol% composite containing intra-granular ZrO_2 particles studied by Heuer *et al.* might also be time dependent [5]. We postulate that microcrystals have a lower M_s temperature in the absence of microcrack precursors compared to those that do have such nuclei. Annealed critical microcrystals at room temperature would develope nuclei in time in the same way as supercritical particles extend microcracks.

A serious difficulty with the nucleation theory as proposed in the recent literature is that it predicts a larger value of d_c for t-ZrO_2 precipitates in Ca–PSZ compared to inter-granular particles in Al_2O_3–ZrO_2 alloys because the thermal expansion mismatch between matrix and precipitate is significantly less than it is in the composite. Consequently the lower non-hydrostatic stresses generated in the precipitates would require a larger value of d_c for transformation at a given M_s. In reality, however, d_c for Al_2O_3–ZrO_2 materials, at room temperature, is ~ 8 times larger than is the case for Ca–PSZ. The problem with the nucleation model is that it tends to be almost a macroscopic approach to events which occur on an atomistic scale. Nuclei must be exceedingly small and transient – of the order of a few unit cells – because after decades of research not a single one has been observed. It is not easy to appreciate how matter on this scale could be influenced by the presence or absence of facets in particles approaching one micrometre in diameter. What is required is a model which is atomistic in nature and can logically treat nuclei of similar dimensions.

The localized soft mode (LSM) theory based on theoretical and experimental studies of martensitic transformations in metals is based on such a model [25]. The heart of the LSM theory is the concept of the strain spinodal. This is a surface of instability in strain space in which the lattice can spontaneously lower its free energy by phase separation into regions of greater and lesser strain, by analogy with the chemical spinodal. The spinodal is a consequence of including an harmonic elastic term in the free energy description of the crystal. Special regions such as the neighbourhood of dislocations, free surfaces and grain boundaries are characterized by stress-free strains which can bring the lattice to the strain spinodal and induce the transformation. A class of lattice vibrations in these regions will behave very differently from the way they do in the unstrained lattice. The anomalous vibrations will have a much larger amplitude of vibration and a much larger persistence time (period) than they have in the bulk. (The amplitude of surface atoms has been measured to be about twice that of bulk atoms [26].) The reason is that the combination of elastic constants that determines the restoring force for this class of vibrations approaches zero as the strain spinodal is approached.

The regions near the stress-free strains are postulated to be the martensitic embryos. They have the required property of being a group of atoms present in the high temperature phase that are frozen into an arrangement somewhat resembling the low temperature phase. The LSM theory predicts that free surfaces, dislocations and grain boundaries would be the easiest sites for heterogeneous nucleation of a martensitic phase. This prediction has been strikingly confirmed by recent experimental work in metals. Galligan and Garosshen successfully separated the nucleation and growth stages of the martensitic transformation in an Fe–Ni alloy [27]. The number of platelets of martensite formed at M_s was directly proportional to the temperature from which the samples had been quenched, but the incubation time required before the onset of transformation was inversely proportional to the quenching temperature. At high temperatures vacancies were quenched in, which eventually, during the incubation period, formed dislocation loops at the M_s temperature. When the loops formed, the transformation proceeded. Such loops were the sites of stress-free strains which allowed the transformation to proceed. The same authors in another study observed plates and/or precipitates of martensite originating in grain boundaries [28]. Easterling and Swann prepared iron-rich, coherent and defect-free precipitates in a copper matrix, 0.002 to 0.2 μm in diameter [29]. Constrained precipitates did not transform unless they were intersected by dislocations introduced by plastically deforming the samples. However, transformation occurred spontaneously in all precipitates which were extracted electrolytically from the matrix. These series of experiments strongly support the LSM theory which required a free surface, grain boundary or a dislocation to nucleate martensitic transformations.

The results of the thermodynamic analysis for Ca–PSZ are in accord with the spirit of the LSM theory; t-ZrO_2 precipitates must be near their coherency limit for transformation to occur. When coherency is lost the high energy of the stress-free strains associated with the dislocations allows the formation of large amplitude, low frequency phonons which begin the transformation. We suggest that the dislocations in CSZ are sufficiently mobile to accommodate the shear strains of the growing nucleus as the matrix is not a very hard ceramic.

According to the results of the thermodynamic analysis the particle–grain boundary interface does not allow the transformation to occur in Al_2O_3–ZrO_2 composite. This is contrary to the prediction of the LSM theory. We speculate that with such a hard matrix dislocations at the interface are immobile and cannot allow the transforming particle to surmount its shear strain energy; the higher energy state of a free surface is a prerequisite for transformation in this case. It seems that microcracking must be concurrent with the transformation occurring in the bulk at low temperatures in the Al_2O_3–ZrO_2 system. At higher temperatures, the mobility of the dislocations could be increased such that microcracking would not be required.

The LSM theory stipulates that the nature of the interface between the transforming particle and its matrix is the controlling factor in the nucleation and growth of the new phase. For Ca–PSZ loss of coherency is the nucleating event and in Al_2O_3–ZrO_2 composites it is the formation of a radial microcrack. These nucleating events are bound up in the total interfacial energy change of the transformation.

It is worth noting that there are hints that soft modes could be involved in the t → m transformation in ZrO_2. The increase of M_s with increasing HfO_2 content of the ZrO_2–HfO_2 solid solution series was interpreted quantitatively on the basis of a soft mode model [30]. Also it has been shown that manipulations of the Lindemann theory of melting (based on lattice instabilities) produce the relationship $(T_b/T_m)^{1/2} \sim 0.8$ for a martensitic transformation where T_m is the melting point [31]. The value of this ratio for ZrO_2 is ~ 0.7.

The ideas in the previous discussion can be tested by obtaining r_c/M_s data for the t → m transformation occurring in a variety of matrices. We predict that for inter-granular particles with hard matrices the $1/r_c$ against M_s plots would be essentially parallel to the plot for the Al_2O_3–ZrO_2 material but with intercepts dependent on the thermal expansion mismatch between particle and host. For softer matrices that do not require microcracking the slopes will be somewhat steeper than that observed for the Ca–PSZ alloy, as there is no loss of coherency. An example of such behaviour should be observed for the ZnO–ZrO_2 composites in which no microcracking was observed after transformation occurred [32]. A programme is under way in this laboratory to obtain such data.

4. Conclusions

1. The observed M_s dependence on the particle size for the t → m transformation occurring in Ca–PSZ, Al_2O_3–ZrO_2 and mullite–ZrO_2 composites can be rationalized by a conventional thermodynamic analysis which includes changes in the bulk chemical and strain energies and also interfacial energies.

2. The factor which controls the initiation of the transformation is the change in energy of the particle–matrix interface.

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