

Intrinsic size dependence of the phase transformation temperature in zirconia microcrystals

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It is argued that because the tetragonal (t) to monoclinic (m) transformation in zirconia is exothermic, this guarantees that the surface free energy of the former is less than that of the latter structure. It is argued further that for pristine, unconstrained, single crystals, $A_s \sim M_s \sim 1447$ K. It follows then, from a thermodynamic analysis that the reciprocal crystallite size is a linear function of the transformation temperature. Quantitative agreement was obtained between calculated and experimental crystallite size-temperature data which ranged over three orders of magnitude.

1. Introduction

For sometime we have argued that the tetragonal \rightarrow monoclinic (t \rightarrow m) transformation temperature (M_s) of ZrO_2 is subject to an intrinsic size effect in pure, unconstrained crystals [1, 2]. Normally, the (unquenchable) high temperature t-phase is stable only above about 1174°C [3, 4]. However, this structure exists indefinitely at room temperature in microcrystals of about 10 nm diameter. The microcrystals need to be unconstrained single crystals which can be prepared by either hydrothermal methods in which the crystals are grown to the critical size from initially subcritical amorphous materials or else by comminution of course, supercritical m-powders [5, 6].

The size effect is guaranteed by the fact that the t \rightarrow m transformation is exothermic [7]. This means that the cohesive energy of a t-crystal is a little less than it is for the m-structure by an amount approximately equal to the heat of transformation. Clearly it will be slightly easier to cleave t-crystal along a particular plane compared to when it has the m-structure; this is merely one way of stating that the surface free energy of t- ZrO_2 is less than that of m- ZrO_2 . If a large m-crystal is subjected to a process of sub-division, competition will ensue between the change in bulk chemical (Helmholz) free energy and surface free energy associated with the transformation. At some point, as the ratio of surface atoms to bulk atoms approaches a critical value, the t-form will be stable even at some temperature, $T \ll T_b$, where the latter quantity is the transformation temperature of an "infinite" crystal. The discussion can be quantified by equating to zero the total change in free energy of a microcrystal, ΔF_0 . Thus, for a spherical crystal of radius, r :

$$\Delta F_0 = 4/3\pi r^3 \Delta F_{chem} + 4\pi r^2 \Delta S_{chem} = 0 \quad (1)$$

where ΔF_{chem} and ΔS_{chem} refer to the change in free energy per unit volume and per unit area, respectively,

associated with the t \rightarrow m transformation. The subscript c denotes a critical value. If ΔF_{chem} is expressed in terms of the experimental variables, q (heat of transformation) and T (transformation temperature $\equiv M_s$) it follows that

$$r_c^{-1} = \left[\frac{q}{3\Delta S_{chem} T_b} \right] T - \left[\frac{q}{3\Delta S_{chem}} \right] \quad (2)$$

Both q and ΔS_{chem} have been measured calorimetrically, making it possible to plot Equation 2 and compare the curve with experimental data [7, 8].

It is worth noting that the form of Equation 2 is invariant when it is applied to constrained crystals. The thermodynamics of the transformation is similar but more complicated. The dilatational and deviatoric transformational strain contribute an amount, $\Sigma \Delta F_{str}$ to the bulk energy term in Equation 1 whilst twinning, loss of coherency or microcracking contribute to the interfacial energy term. In the general case, the transformation can occur in the presence of an applied stress, W_a , so that Equation 2 becomes

$$r_c^{-1} = \left[\frac{q}{3\Sigma \Delta S T_b} \right] T - \left[\frac{q + \Sigma \Delta F_{str} + W_a}{3\Sigma \Delta S} \right] \quad (3)$$

Equation 3 has been discussed in detail elsewhere [9].

To use Equation 2 sensibly requires an operational definition of T_b . The difficulty is that studies of the transformation in powders show it to be athermal, occurring over a wide temperature range and to display considerable hysteresis between the heating and cooling directions [10]. The problem can be solved and T_b defined operationally by considering the results of experiments on pristine single crystals presented in Table I [3, 4]. The first four lines are the results of Ono who determined the temperature of the transformation in both directions (t \rightleftharpoons m) using flux-grown pristine crystals [3]. The crystals were grown at various temperatures and then cooled to room temperature. Although all crystals were m-phase at room

TABLE I Transformation temperature of pristine single crystals

Method	Temperature (°C)	Morphology
Flux grown (PbF ₂) sealed tube	1180 ± 10	t
Same as above	1130 ± 10	m
Flux evaporation, Borax	1140 ± 10	m
Same as above	1165 ± 10	t
Flux and hydrothermally grown	1174 ± 6	m → t

temperature the structure which prevailed at the growth temperature was established from the external, macroscopic symmetry of the crystals. Of the growth temperatures studied, the highest temperature at which the m-structure was stable was 1140 ± 10° C, whilst the lowest temperature at which the t-structure was stable was 1165 ± 10° C. Presumably, if the experiment were extended to include finer gradations of the growth temperature intervals, these limits would converge to a common value; i.e. for pristine single crystals, hysteresis is negligible and $M_s \sim A_s = T_b$. Mitsuhashi and Fujiki directly observed the m → t transformation in 60 pristine crystals prepared either by hydrothermal or flux methods and determined that $A_s = 1174 \pm 6^\circ\text{C}$ ($= T_b$) where the standard deviation refers to the whole population of crystals [4]. For any particular crystal there was no athermal feature; the width of the transformation < 0.1° C and was very rapid. However, during cooling and after transformation, the mean M_s value was 1085° C and occurred over a temperature range of 40 to 50° C for any particular crystal. Cycled m-crystals were opaque due to a high density of cracks.

In summary, the transformation in large pristine single crystals is not athermal, occurs rapidly over a narrow temperature range and displays negligible hysteresis. Under these conditions T_b is well-defined and is assigned the value of 1174° C from the data in Table I. If M_s or A_s differ significantly from this value the variation will be due to a definable physical or chemical effect. By way of contrast the transformation in polycrystalline powders is athermal with the transformation occurring over a range of up to about 125° C and displaying a hysteresis width of 200° C or more [10]. These features are due to the broad particle size distribution, typical of any powder and to the effect of the transformational strains of one crystallite on its yet to be transformed neighbour. A detailed interpretation requires an account of the mechanism of hysteresis which is treated elsewhere [11]. During cycling through the inversion, an initially single crystal of m-ZrO₂ forms an aggregate of aligned mosaic blocks due to the transformational strains. In effect the material has become polycrystalline and so displays the features characteristic of the transformation in polycrystalline powders. Examination of the values of A_s in the literature for m → t for a range of powders show that they are close to the assigned value of T_b . There is a sound reason for these observations to which only allusion can be made here. During cooling of a polycrystal the t → m transformation is described by an equation of the form of Equation 3 (with $W_a = 0$) in that a strain term is involved. However,

during heating the appropriate equation to use would be one similar to Equation 2 without any or a much reduced strain term. This is the physical basis for the phenomenon of hysteresis. The argument is subtle, requiring separate discussion [11]. The outcome is that A_s measurements of polycrystals or constrained crystals are equivalent to measurements of T_b , the thermodynamic transformation temperature of an unconstrained crystal of size, r_c , provided that its interface is always free or incoherent [11]. It is believed that this condition is met by the materials used in this work, as discussed below.

The purpose of this contribution is to provide evidence to test Equation 2. This can be done by measuring A_s , for a series of powders of a narrow size distribution in which the particles are either single crystals or coarsely twinned. During heating the powder fractions with smaller mean sizes will sinter but A_s will be an acceptable approximation of the true transformation temperature, T_b , as discussed above.

2. Experimental details

The material used was powdered baddelyite, because each particle was either a single crystal or coarsely twinned (J. Drennan, private communication). The size distribution of the as-received powder ranged from 50 to 1 μm with a mean value of 8 μm. Four samples of powder were prepared, as follows. A coarse sample with a distribution ranging from 20 to 5 μm and a mean size of 9 μm was fractionated from the as-received powder using an Acucut A12 classifier. The as-received powder was then ball-milled in water for 16 h to produce a powder with a mean size in the range 2 to 3 μm. This powder was next classified by gravity sedimentation into three samples of nominal size 1, 0.5 and 0.15 μm, respectively. The sedimentation medium was isopropyl alcohol. The settling times and heights to produce each fraction was calculated using Stokes law [12]. The size distribution of each fraction (except the finest because of insufficient material) was measured using a Sedigraph 500ET particle size analyser. A visual check was made of the size distribution of each fraction from SEM micrographs. The A_s temperature of each fraction was measured using DTA. The value of A_s was defined as the intersection of the baseline with the tangent to the rising segment of the DTA peak [13].

3. Results and discussion

The heat of transformation, q , and the difference in surface free energy of the two polymorphs of ZrO₂ amount to 594 kJ mol⁻¹ (\equiv 282 MPa) and 0.36 J m⁻², respectively, as measured calorimetrically [7, 8]. Using these values in Equation 2, along with the value of $T_b = 1174^\circ\text{C}$ yields the linear plot shown in Fig. 1. The mean particle size of the various fractions estimated from the frequency distribution curves (Fig. 2) and the scanning electron micrographs (Fig. 3) is 9, 0.85, 0.4 and 0.17 μm, respectively. These values are plotted in Fig. 1 as a function of A_s ($\equiv T_b$), the latter values having been determined by DTA. There is good agreement with the calculated curve. The value of T_b measured for the 9 μm size fraction was the same as

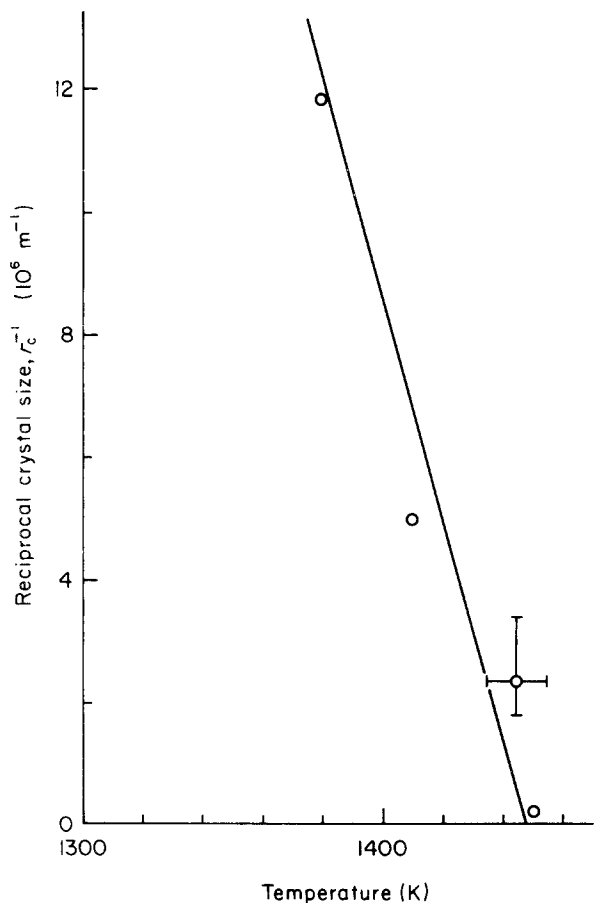


Figure 1 Experimental and calculated temperature dependence of the reciprocal crystallite size, r_c . The error bars are one standard deviation.

that estimated from Table I, within experimental error. The values of M_s were less than that of A_s for all samples because they were converted from single crystals to polycrystalline powders. The particles in the coarse fraction with mean size $\sim 9 \mu\text{m}$ would break up with cycling whilst the fine fractions (mean size = 0.8 to $0.17 \mu\text{m}$) would sinter during the heating sector of the DTA runs.

Fig. 4 presents results for the critical size at room

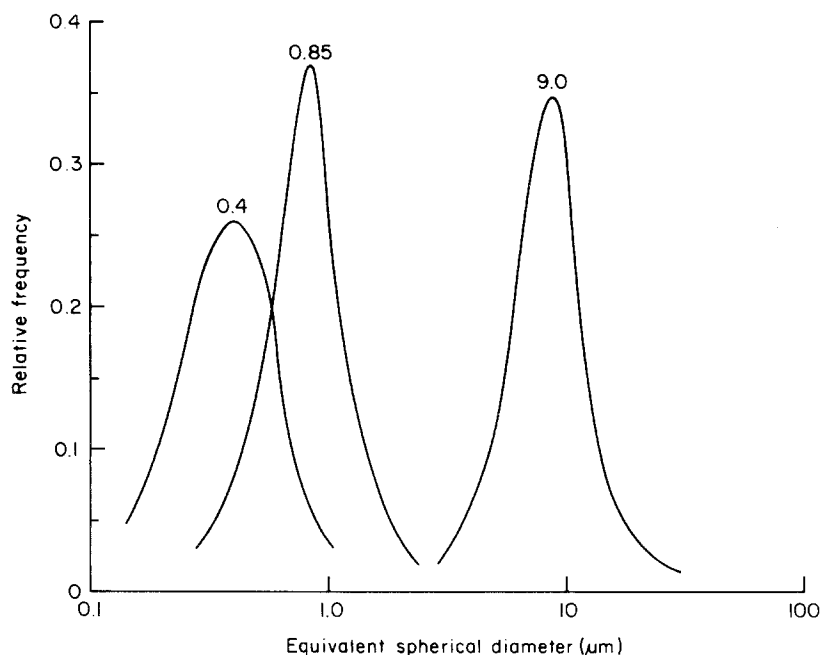


Figure 2 Particle size distribution of the classified powders.

temperature obtained by vibro-milling coarse m-crystals (solid circle) and hydrothermal growth of amorphous zirconia (half-solid circle) [5, 6]. Bailey *et al.* vibromilled m-ZrO₂ powders for up to 50 h and observed the spontaneous occurrence of t-ZrO₂ when the size was about 9.7 nm [6]. This value is the average of the largest m- and the smallest t-particles observed and is in remarkable agreement with the calculated value (solid line). Mitsuhashi *et al.* [5] arrived at the critical size from the opposite direction, by the hydrothermal growth of amorphous powders at a pressure of 1 kbar and temperature in the range 235 to 245°C for the time periods of 10 to 55 min. The critical diameter at room temperature for strain-free single crystals was 10 nm, again in excellent agreement with the calculated value. We regard the agreement between the two experimental values in which the critical size was approached from opposite directions, combined with their confirmation of the theoretical value, based only on calorimetric data, as strong evidence for the existence of an intrinsic size effect in the $m \rightleftharpoons t$ transformations in zirconia. The fact that there is good agreement between the experimental and calculated values over a range of three orders of magnitude for the particle size (Fig. 4) further strengthens the case presented here.

There are examples in the literature which seem to contradict the idea that an intrinsic size effect exists which controls T_b . However, careful scrutiny of the data usually shows that some extraneous factor is responsible. For example, chemical effects can influence the critical size, probably by altering the surface free energy difference of the two forms. Bailey *et al.* [6] noted that additions of either HCl or NaOH during vibromilling inhibited the formation of the t-phase. Morgan [14] prepared 6 nm m-crystals by ageing a mixture of zirconyl nitrate and concentrated HNO₃ solutions in a bomb at 150°C. A reduction in the surface free energy difference from 0.36 to 0.22 J m^{-2} would account for this effect. The formation of polycrystals tends to increase the value of the critical size,

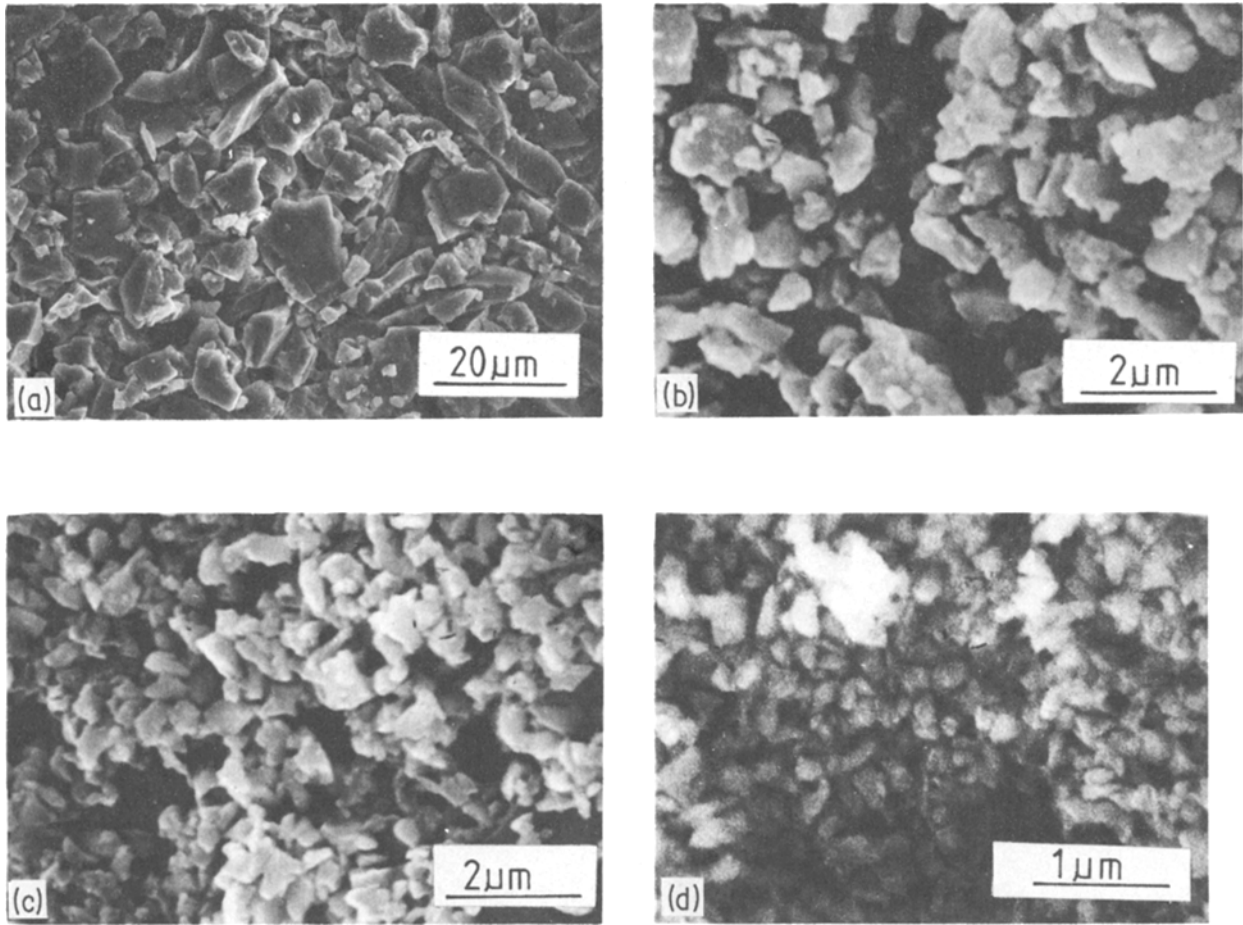


Figure 3 Scanning electron micrographs of the classified powders. Mean size: (a) 9 μm ; (b) 0.85 μm ; (c) 0.4 μm ; (d) 0.17 μm .

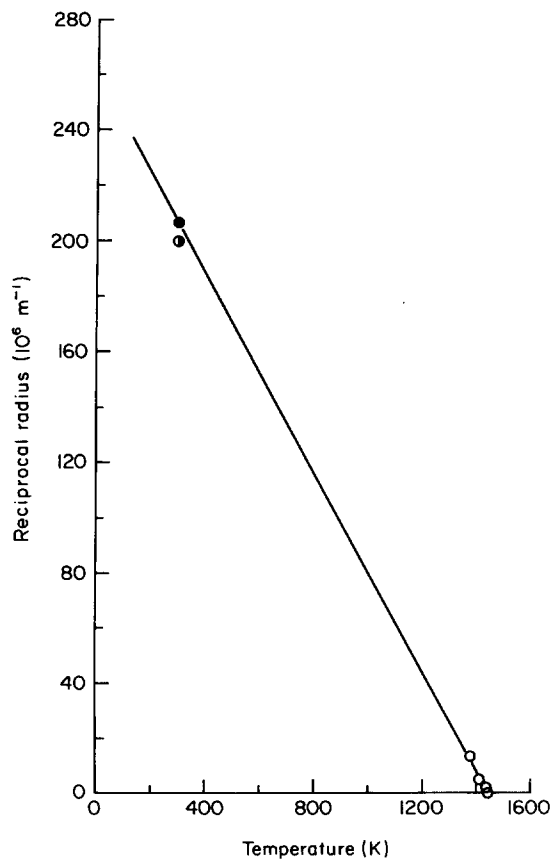


Figure 4 Intrinsic size effect in milled and in hydrothermally grown crystallites.

as shown by the interesting observations of Bailey *et al.* on annealed, milled powders which was inexplicable at this time [6]. The starting powder had a mean size of 10 nm and a t-phase content of 45% which is depicted schematically in Fig. 5a on the assumption that there is an appreciable range of sizes, distributed normally. When the powder was annealed in the range 600 to 800° C, there was little change in the crystallite size but the t-phase increased to 75 to 80%. It is probable that light sintering occurred during annealing so that during cooling the crystallites would experience deviatoric strains and the critical diameter is given by

$$d_c^{-1} = \left[\frac{q}{6\Sigma\Delta ST_b} \right] T - \left[\frac{q + \Delta F_{\text{dev}}}{6\Sigma\Delta S} \right] \quad (4)$$

where the interfacial term, $\Sigma\Delta S$, includes a contribution from twin boundary formation [9]. Upon inserting the appropriate values in Equation 4, the value of d_c at room temperature now amounts to 27 nm causing an increase in the amount of t-phase (Fig. 5b) [9]. When annealed at 1000° C, the crystallite size increased to ~ 51 nm with a fall in the value of the t-phase content to 20%. This particle growth would be accompanied by extensive sintering so that dilational strains would be generated by transforming crystallites, adding ΔF_{dil} to the strain energy term in Equation 4 [9]. The new value of d_c is ~ 40 nm, resulting in a decrease in t-zirconia (Fig. 5c). Mitsuhashi *et al.* [5]

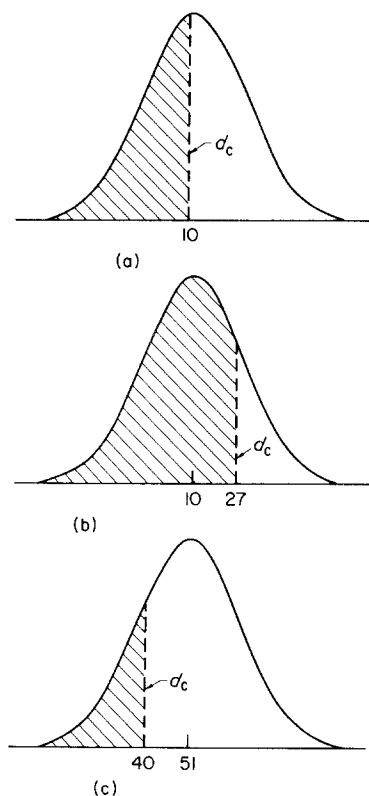


Figure 5 Schematic particle size distribution curves of annealed, milled powders. The shaded area is tetragonal. (a) No annealing, (b) annealing 600 to 800°C, (c) annealed 100°C. Crystal size in nm.

examined strained polycrystals of ~ 200 nm diameter comprised of crystallites $\sim 46 \pm 10$ nm and showed that the latter had t-symmetry, in accord with the present analysis.

Chen and Chiao [15] prepared t-ZrO₂ microcrystals by the internal oxidation of zirconium particles dispersed in a copper matrix. Oxidation was carried out in the range 740 to 960°C, producing zirconia particles with diameters mainly in the range 30 to 100 nm. Oxide particles prepared near the higher end of the temperature range had the t-structure whilst those which had been oxidized near the lower end, more frequently had the m-structure. These authors simultaneously argued against any intrinsic size effect and affirmed the transformation temperature of their microcrystals to be $\sim 950^\circ\text{C}$ [15, 16]. This cannot be so in the light of the data presented in Table I. In the absence of any size effect, the microcrystals were formed in the field of stability of m-ZrO₂ and they ought to have been formed with that structure. This comment applies to the formation of microcrystalline t-ZrO₂ in general at temperatures $< T_b$; why does t-ZrO₂ form at all under this condition when the crystal can adopt whatever is the stable structure at the temperature of formation? The onus is on opponents of the views presented here to provide a satisfactory answer to this question. The thermodynamic approach can account for the observations of Chen and Chiao as follows. Again, the equation to use is similar to Equation 4 except that the transformational strain energy is negligible because of the ductility of the matrix. The critical size at 740°C is 55 nm which increases to 112 nm at 960°C. If the observed range of particle sizes (30 to 100 nm) is distributed normally then mainly t-particles would be formed at 960°C,

whilst at 760°C, the frequency of formation of m-particles would increase, in accord with the experimental results.

The low probability of finding a suitable nucleating site on a small particle is frequently involved to explain the occurrence of t-ZrO₂ at low temperature [15–17]. Difficulty of nucleation can account for the persistence of the t-phase but not its initial formation when the temperature of formation is in the stability range of the m-phase. For example, Misuhashi *et al.* [5] prepared stable pristine single crystals of t-ZrO₂ ~ 28 nm diameter $> d_c = 10$ nm by slow hydrothermal growth at 215°C and 1 kbar for 22 h [5]. The temperature of abrupt crystallization is $235 \pm 10^\circ\text{C}$. The surfaces formed under the condition of slow growth would be comparatively free of flaws and the transformation more difficult to nucleate. Chen and Chiao [15] also showed that their 30 to 100 nm diameter t-crystals which were free of surface flaws were stable at room temperature, even when removed from the matrix. However, transformation was induced when the composite material was cold-worked.

4. Conclusions

1. The $m \rightleftharpoons t$ transformation in zirconia is reversible in the thermodynamic sense and in principle characterized by a single, sharp temperature, $T_b = 1447 \pm 6^\circ\text{C}$ for the special case of pristine, large and unconstrained single crystals.

2. The fact that the $t \rightarrow m$ transformation with cooling is exothermic guarantees the existence of an intrinsic size effect such that the reciprocal crystallite size is a linear function of the transformation temperature, $T(\equiv M_s)$.

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