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Time-dependent tetragonal to monoclinic transition in hot-pressed zirconia stabilized with 2 mol % yttria

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The kinetics of isothermal transformation from tetragonal (T) to monoclinic (M) structure in zirconia stabilized with 2 mol % yttria was systematically studied using thermal expansion analysis, electron probe microanalysis, X-ray diffractometry and transmission electron microscopy. Results showed that tetragonal phase obtained from rapid cooling transforms isothermally to monoclinic phase during holding at 200–400 °C for 4 h. The time–temperature–transformation (TTT) curve has a characteristic C-shape, with 300 °C as the "nose" temperature. A small amount of M phase can be detected when the holding temperature is not in the preceding temperature range. The isothermal transformation kinetics can be expressed in terms of the Johnson–Mehl–Avrami equation in which the nucleation and growth of new phase are both functions of time with the activation energy determined to be 28.67 KJ mol^{-1}. The metastability of T phase is associated with cooling rate, stabilizer content, as well as grain size. *In situ* observation of M phase propagation induced by the electron beam reveals the T → M transition to be diffusion controlled.

1. Introduction

Zirconia possesses polymorphic structure, namely, cubic (C), tetragonal (T) and monoclinic (M) phase, from high to low temperature, respectively. Pure zirconia is of little engineering value owing to bulk disintegration caused by T → M martensitic transformation [1]. Stress-induced T → M transformation in partially stabilized zirconia (PSZ) or tetragonal zirconia polycrystals (TZP) is the origin of toughening during which the tip of a propagating crack can be shielded by the resulting stress field. Metastability of T phase is affected by such factors as the content of stabilizer, surface energy, constraint of the matrix, grain size, as well as the difficulties of nucleation [2–4]. Earlier studies [5] on isothermal conversion from T to M in yttria-containing zirconia disclosed it to be isothermal martensitic transformation in which nucleation is related to thermal activation. The concept of a Banite-like transformation in the T → M transformation has recently been proposed [6], the preciseness of which, apparently, needs to be further explored. The aim of the present work was to elucidate the mechanism of isothermal T → M transformation in hot-pressed ZrO_2(2 mol % Y_2O_3).

2. Experimental procedure

Zirconia doped with 2 mol % yttria was hot pressed at 1600 °C under a pressure of 25 MPa with 1 h holding time, followed by water cooling. Elimination of post-sintering stress was carried out by heating the sintered body to 800 °C for 5 h during which the growth of grains could be neglected. Samples for the inspection of the grain-size effect were fabricated by pressurelessly sintering the green body formed under a pressure of 300 MPa. The fraction of monoclinic phase was calculated using the formula suggested by Porter [7]. Thermal expansion analysis (TEA) was performed using a Perkin-Elmer 7 Series Thermal Analysis System with a sample machined to the size 3 mm × 3 mm × 4 mm. The sample for transmission electron microscopy was prepared by the conventional argon-ion thinning procedure, while observation was made at H-800 microscopy operated at 200 kV.

3. Results and discussion

3.1. Metastability of T phase and affecting factors

Fig. 1 shows the thermal expansion curves obtained for different heating and cooling rates, which reveals that the T → M transformation is very much influenced by both these rates, whereas the M → T transition remains almost unaffected by heating rate. The total amount of expansion due to the T → M transformation occurring during either heating or cooling, decreases with increasing heating or cooling rate. Even when the heating rate reaches 60 °C min^{-1}, there is no extra expansion incurred by the T → M transformation during heating, implying that the T → M conversion has been suppressed. Furthermore,

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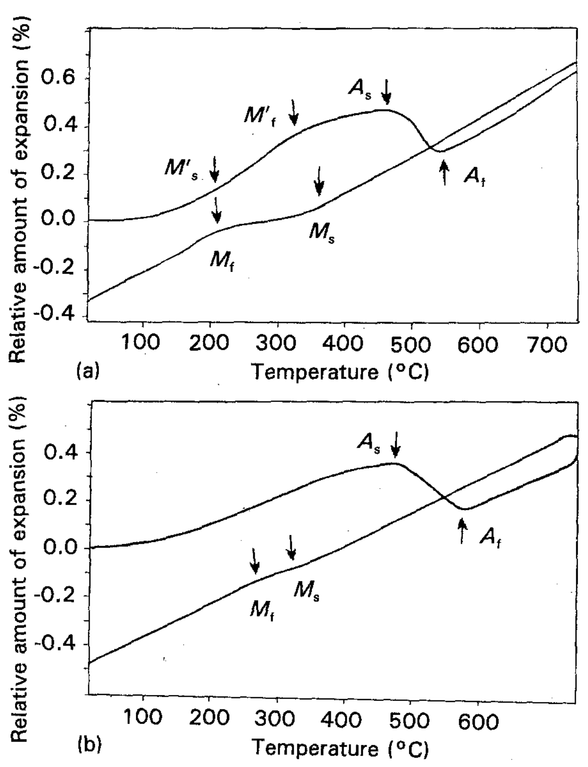

Figure 1 Relative amount of thermal expansion versus the change of temperature with different heating and cooling rates. (a) 10 °C min^{-1}, (b) 60 °C min^{-1}.

the temperature range experienced by the T → M transformation during cooling becomes narrower as the cooling rate increases.

A_s and A_f (starting and ending temperatures of the M → T transformation, respectively) both shift to high temperature when the heating rate increases, while M_s (starting temperature of the T → M transformation) decreases with increasing cooling rate; however, M_f (ending temperature of the T → M transformation) follows the opposite trend, M'_s and M'_f are the starting and ending temperature of the T → M transformation during heating, respectively. The T → M transformation proceeds within a certain temperature range measured to be about 200–400 °C beyond which no M phase can be detected. It is evident that the generation of M phase is not only temperature-related but also time-dependent. The dependence of M_s on cooling rate is undoubtedly attributable to the time effect of nucleation of transformation which can be completely inhibited by a sufficiently rapid cooling.

One of intrinsic elements controlling the amount of retained T phase is the solute content. Different grains contained different levels of dopant due to rapid cooling after sintering as well as a short holding time during sintering. For a sample to reach the equilibrium composition represented by the phase diagram, prolonged annealing in the T phase region with the avoidance of grain growth, is required. The critical cooling rate required to suppress the appearance of M products is inversely proportional to the yttria content, i.e. the higher the yttria content, the smaller the critical cooling rate should be. Table I lists the EPMA results of yttria content in different grains, which confirms the present argument that the yttria content varies with the tetragonal grain in hot-pressed zirconia. Moreover, yttria content is virtually inhomogeneously distributed even in the same grain, which is one of the reasons for the existence of dual phase (T + M), favouring the determination of the orientation relationship between the T and M phases.

TABLE I EPMA results of yttria distribution in different tetragonal grains

Grain	Yttria content (mol %)
1	1.43
2	2.22
3	1.87
4	1.94

The stability of the T phase has already been established to be grain-size dependent, for which different authors give different explanations [2, 4, 8, 9]. Fig. 2 shows the relationship between the fraction of monoclinic phase and grain size, in which the critical grain size of 0.5 μm can be readily obtained. It can be seen that when the grain size is larger than 0.5 μm, the fraction of M phase increases exponentially with grain size. The curve is likely to fit the following formula

$$f = 1 - \exp(-cD^n) \quad (1)$$

whereas f is the fraction of M phase, D is the grain size of T phase, and n the exponent determined to be between 2 and 3. The implication of n is worth further study. In fact, nucleation of M phase often preferentially occurs at such heterogeneous sites as dislocations, stacking faults and grain boundaries, which has been confirmed by TEM observation. Dislocations and stacking faults in T phase are readily discerned with the appropriate operating vector $\boldsymbol{g}$. Fig. 3 gives the configuration of a group of dislocations with [0 0 1] as Burger vector [10]. The number of heterogeneities is believed to increase with grain size, as does

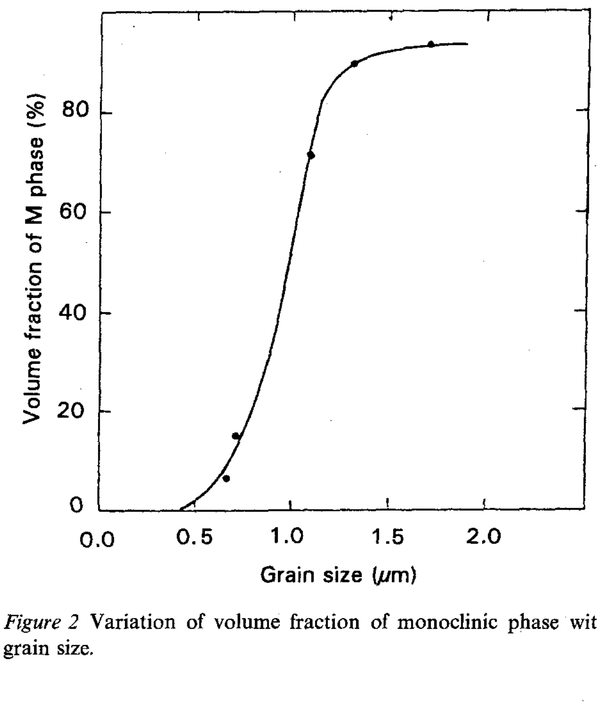

Figure 2 Variation of volume fraction of monoclinic phase with grain size.

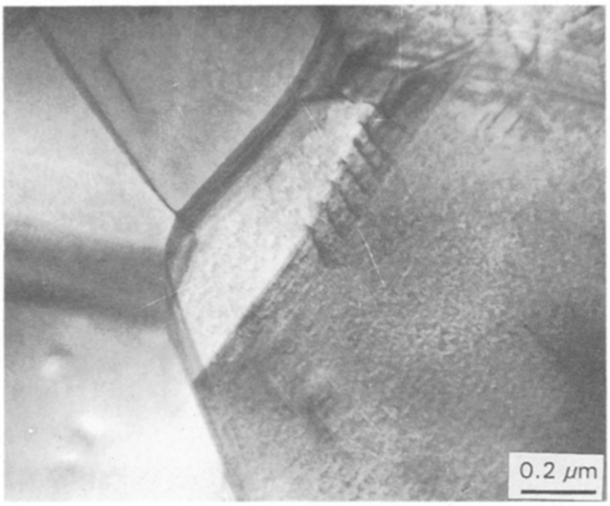

Figure 3 Photograph of a group of linear dislocations with [0 0 1] as Burger vector.

that of the critical nucleus. In addition, an increase in defects is beneficial to the diffusion of oxygen vacancies and ions, in that defects presumably decrease the activation energy barrier.

3.2. Isothermal kinetics of T → M transformation

Variation of the amount of M phase formed at different holding temperatures with holding time is typical of a sigmoidal curve, as shown in Fig. 4, which indicates that the T → M transformation proceeds isothermally. The tendency for isothermal transformation can also be inferred from Fig. 1 during the heating stage, particularly when the heating rate is small (10 °C min^{-1}), i.e. an expansion phenomenon around 200–400 °C. Metastable T phase is obtained prior to holding in such a way that T → M transformation is totally restrained through rapid cooling (100 °C min^{-1}). The corresponding time–temperature–transformation (TTT) curve is shown in Fig. 5.

The present results on isothermal kinetics establish that

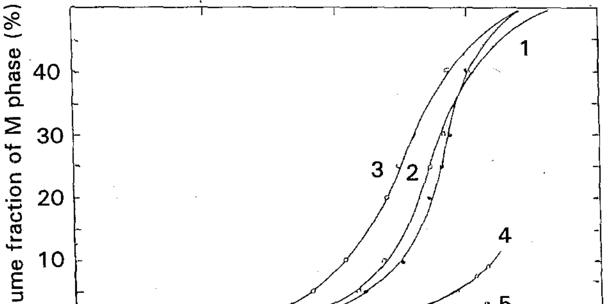

Figure 4 Change of volume fraction of monoclinic phase formed at different holding temperatures with holding time. (1) 473 K, (2) 523 K, (3) 573 K, (4) 623 K, (5) 673 K.

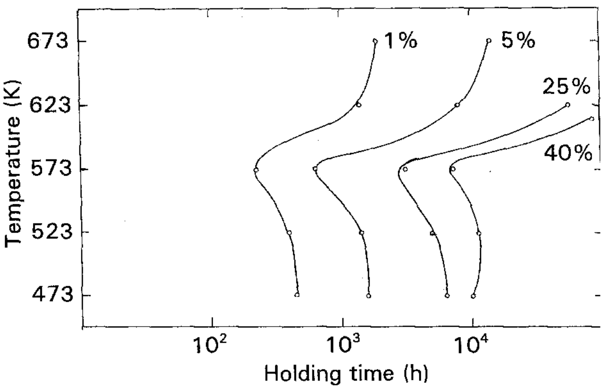

Figure 5 Corresponding time–temperature–transformation (TTT curve.

(i) the existence of an incubation period which initially becomes shorter with decreasing holding temperature, then becomes longer when the holding temperature is further decreased, results in the appearance of a "nose" temperature determined to be abou 300 °C. The existence of an incubation period is one of the features of diffusional transformation whose isothermal kinetics can be expressed in terms o the Johson–Mehl–Avrami (JMA) equation, i.e $f = 1 - \exp(-kt^n)$, where f is the volume fraction o transformed phase, k is a variable associated with the energy barrier for critical nucleation and growth, and n is a constant depending on the nucleation sites;

(ii) at the initial stage of transition, the transition rate (df/dt) is small, but becomes bigger as transformation proceeds, until the end of transformation;

(iii) the value of n, the exponent in the JMA equation, is determined to be 1.26 when the holding temperature is within the range 200–300 °C, beyond which n becomes smaller, implying that the nucleation sites might have changed with increasing holding temperature (Fig. 6);

(iv) the functional relationship between the ln(nk and $1/T$ shown in Fig. 7 reveals the activation energy

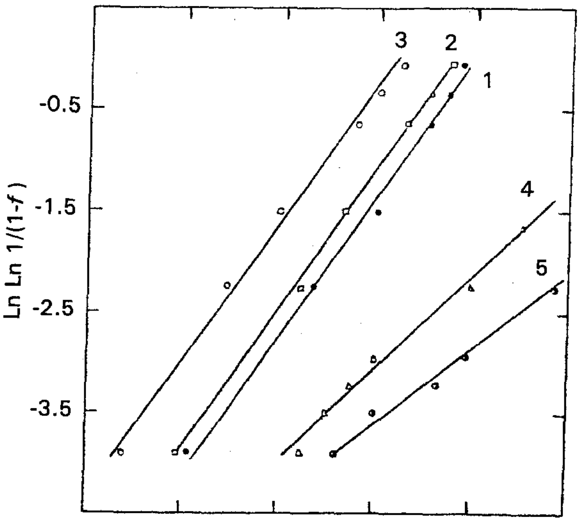

Figure 6 Linear relationship between lnln 1/(1 − f) and ln t at different holding temperatures, (1) 473 K, (2) 523 K, (3) 573 K (4) 623 K, (5) 673 K.

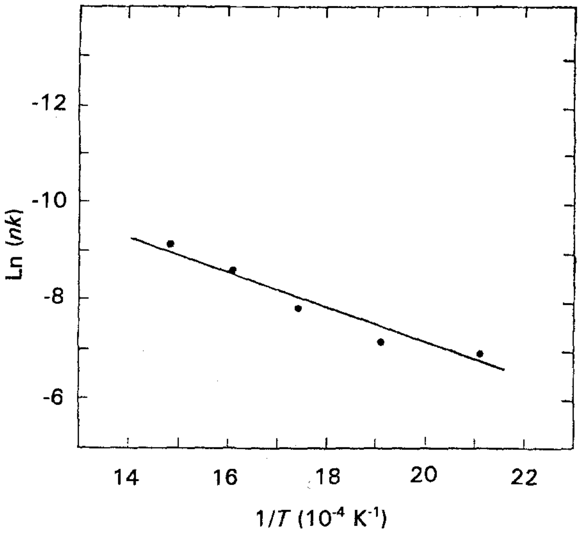

Figure 7 Functional relationship between $\ln(nk)$ and $1/T$.

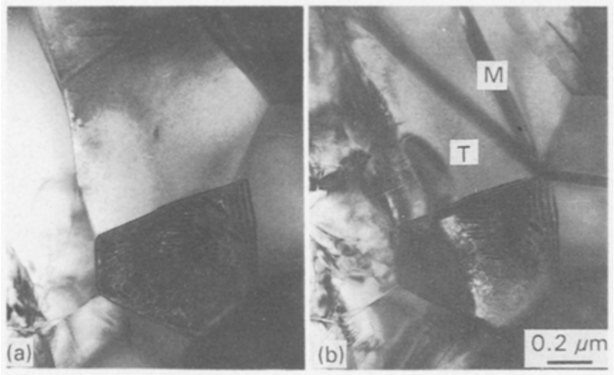

Figure 8 Nucleation of monoclinic plates at a grain corner under the irradiation of an electron beam.

for transformation to be 28.67 kJ mol^{-1} irrespective of the holding temperature;

(v) the isothermal transformation cannot proceed to completion with T + M dual phase as the final microstructure.

3.3. Interpretation of TTT curve

The generation of the TTT curve with a C-shape is undoubtedly attributed to at least two contradicting factors responsible for the nucleation and growth of M phase. Grain boundaries are the most favourable nucleation sites compared with other defects. Fig. 8 shows photographs of simultaneous nucleation of three plates of M phase at a grain corner. However, intragranular nucleation at such defects as dislocations and stacking faults, can be observed, particularly when the driving force is relatively large [4]. For simplicity, we analyse the thermodynamics of nucleation at grain boundaries for the T → M transformation.

σ_1, σ_2 are assumed to be interface energy of T/M and the grain boundary energy of T/T, respectively. A_1 and A_2 represent the area of the T/M interface and the T/T grain boundary, respectively. ΔE is the change in strain energy associated with transformed M phase and surrounding T phase. ΔG_v is the change of chemical free energy between T and M phases, r and V are the radius and volume of the nucleus, respectively. When the transformation occurs, the variation of free energy can be expressed as

$$\Delta G = \sigma_1 A_1 - \sigma_2 A_2 - \Delta G_v V + \Delta E V \quad (2)$$

where $A_1 = ar^2$, $A_2 = br^2$, $V = cr^3$, $a = \pi(1-k^2)$, $b = 4\pi(1-k)$, $c = 2\pi/3(2-3k+k^3)$, $k = \sigma_2/\sigma_1$, then

$$\Delta G = \sigma_1 ar^2 - \sigma_2 br^2 - \Delta G_v cr^3 + \Delta E cr^3 \quad (3)$$

taking $\alpha\Delta G/\alpha r = 0$, therefore

$$r^* = 2(\sigma_1 b - \sigma_2 a)/3c(\Delta G_v - \Delta E) \quad (4)$$

We can obtain the expression for the critical nucleation barrier

$$\Delta G^* = r^{*2}(b\sigma_1 - a\sigma_2)/3 \quad (5)$$

taking some data concerned with pure zirconia [10], $\Delta E = 17.98\ \mathrm{J\,cm^{-3}}$, $\Delta H = 282.61\ \mathrm{J\,cm^{-3}}$, $\sigma_1 = 0.2\ \mathrm{J\,m^{-2}}$, $\sigma_2 = 0.25\ \mathrm{J\,m^{-2}}$, because $\Delta G_v = \Delta T \Delta H / T_0$, $\Delta T = T_0 - T$. The thermodynamic temperature for transformation, T_0, is taken as $(M_S + A_S)/2$; according to dilation results, T_0 is about 723 K. If we take 50 K as ΔT for the time being, and substitute data concerned into Equations 4 and 5, we can calculate ΔG^* to be 15.8 J mol^{-1} which is approximated to be zero compared with the conventional value of the critical nucleation barrier for solid transformation.

Per unit time, per unit volume, the number of stable nuclei can be written as

$$I = wA\exp(-Q/KT)\exp(-\Delta G^*/KT) \quad (6)$$

where w is frequency of ion vibration, A is the area of grain boundaries per unit volume, and Q the activation energy for the diffusion of oxygen ion. Because ΔG^* is so small that it can be neglected, Equation 6 can be rewritten as

$$I = wA\exp(-Q/KT) \quad (7)$$

Equation 7 indicates that nucleation of T → M transformation depends on the diffusion of an oxygen ion as well as the area of grain boundaries per unit volume. In addition to the grain boundaries, dislocations and stacking faults will become the potential nucleation sites with increasing supercooling, therefore the value of A in Equation 7 can be extended to include the volume of dislocations and stacking faults per unit volume. A increases with decreasing isothermal temperature, leading to the fact that the exponent n in the JMA equation also increases with decreasing temperature until 300 °C, when the nucleation sites saturate.

On the other hand, growth of monoclinic phase is equally controlled by the short-range diffusion of oxygen ions and vacancies. Fig. 9 shows the process of *in situ* growth of monoclinic plates under irradiation by an intensive electron beam, which indicates that the T → M transformation is a time-consuming process (time interval from (a) to (b) is about 1 min). Consequently, the generation of the TTT curve with a C-shape is the result of nucleation and growth of

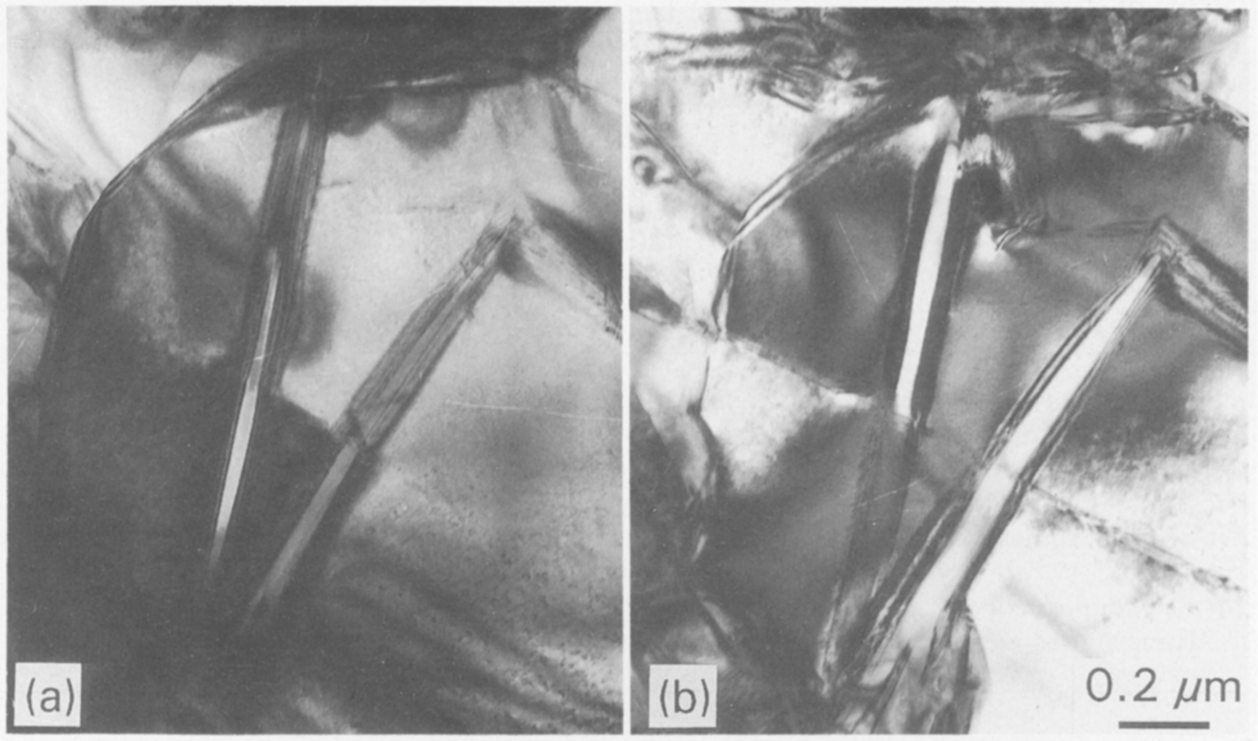

Figure 9 *In situ* growth of monoclinic phase induced by an electron beam.

transformation from T to M structure. The increase of product phase involves the growth of original plates as well as the nucleation of new plates. Nucleation and growth are all thermally activated processes. T → M transformation virtually cannot proceed to completion with the T + M dual phase as the final microstructure due to the fact that constraint imposed on parent phase resulting from the dilational transition from T to M phase increases with the amount of transformed monoclinic phase.

4. Conclusions

1. The T → M transformation in zirconia stabilized with 2 mol % yttria is strongly time-dependent. The curve of time–temperature–transformation (TTT) is C-shaped with 300 °C as the "nose" temperature. The isothermal kinetics can be described in terms of the JMA equation with activation energy regressed to be 28.67 kJ mol^{-1}.

2. The retention of tetragonal phase at room temperature depends on the cooling rate, grain size, as well as the stabilizer content.

3. Both the nucleation and growth of monoclinic phase are associated with the diffusion of oxygen ions which controls the kinetics of transformation.

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