

Effect of zirconia particle size distribution on the toughness of zirconia-containing ceramics

Y. M. LIANG*, J. H. ZHAO†

Department of Modern Mechanics, University of Science and Technology of China, Hefei, Anhui, 230027, People's Republic of China
E-mail: jhzhao@ustc.edu.cn

The zirconia particles in zirconia-containing ceramics have a size distribution similar to Gaussian distribution. The spontaneously martensitic start temperature (M_s) of different particles are not the same. The larger the particle, the higher its M_s . On cooling from high temperature to a value lower than the macro M_s of the materials, the stress-induced and spontaneous transformation will happen, so that the toughness of the materials increases at first, then gradually drops to a value slightly higher than that of the matrix. The size distribution plays an important role in affecting the toughness of the materials. When the average particle size increases, the maximum toughening $(\Delta K_c)_{\max}$ and the temperature (T_{\max}) at which $(\Delta K_c)_{\max}$ happens will all increase. The toughness at given temperature will increase at first and then drop also to a value slightly higher than that of matrix with increasing of average particle size. The stronger concentration of the size distribution, the higher $(\Delta K_c)_{\max}$ will be. The weaker concentration for size distribution (either the range of zirconia particle sizes becomes wider or the scale parameter of the distribution increases), the lower $(\Delta K_c)_{\max}$, but the range of temperature in which the toughness is larger than certain value will become wider. Some suggestions of designing ceramics with high toughness at different temperatures are given. © 1999 Kluwer Academic Publishers

1. Introduction

Transformation toughening of zirconia-containing ceramics has been extensively researched in the last 20 years [1–4]. In these ceramics, the high temperature phase-tetragonal (t) phase of zirconia is retained. It can be transformed to its low temperature phase-monoclinic (m) phase under applied stresses. The $t \rightarrow m$ transformation of free zirconia particles was accompanied by a volume dilatation of about 5% and a shear deformation of about 14%. But when the t -zirconia particles are constrained by matrix (e.g., Al_2O_3), lots of twins will appear during the process of the transformation. These twins will diminish the shear deformation at quite large extent. So, it can be supposed that only volume dilatation accompanies the $t \rightarrow m$ transformation when the particles are constrained by matrix [3]. When these particles are near the crack tip, the volume dilatation will change the stress distribution and weaken the stress concentration near the crack tip and then toughen the materials.

The previous researches [1–4] supposed that all the transformable particles in the materials have the same size. When the crack extends stably, a transformation zone with certain width will appear on both sides of the main crack. The volume fraction of the transformed zir-

conia in the zone is uniform. There is no transformed zirconia out of the zone. But it was found that the volume fraction of the stress induced transformed zirconia in the materials diminishes with increasing of the distance vertical to the crack surface [5–7]; For ceramics with certain composition, the martensitic transformation start temperature (M_s) of the zirconia particles with different sizes are different from one another and the M_s increases as the particle size increases [8]; The width of the transformation zone increases with increasing of the average particle size [8–10]; The yielding or critical transformation stress of ceramics decreases as the average particle size increases [11]. When the temperature decreases to a value lower than the macroscopic M_s of the material, the toughness of the materials is still quite high because of the stress-induced transformation. All these indicate that the sizes of the tetragonal zirconia particles are not the same, and have a size distribution. The condition for the transformation of particles with different sizes are different. Changes of the particle size distribution will influence the properties of the materials, for example: M_s , toughness, etc.

The objective of this paper is to study the effect of the size distribution of the tetragonal zirconia inside the materials on the properties (mainly the toughness and

* Former Ms Student at USTC.

Present address: Dept. of Theor. and Appl. Mech., Univ. of Illinois at Urbana-Champaign, IL 61801, USA.

† Author to whom all correspondence should be addressed.

the relationship between toughness and temperature) of the materials. In Section 2, we will give out a simple relationship between the size of a constrained particle and its M_s . In Section 3, we suppose a size distribution of the t -ZrO₂ inside the materials. In Section 4, considering the size distribution and change of temperatures, we will deduce the equations of transformation toughening. Finally, with a detailed computational sample, we discuss the effect of size distribution on the macroscopic properties of the materials.

2. Relationship between the size of the constrained t -ZrO₂ and its M_s

In 1982, Heuer *et al.* [12] found by experiments that under certain temperature, a critical size r_c exists, above which, all the t -ZrO₂ particles will transform to m -ZrO₂. It is indicated that for the t -ZrO₂ particles with different sizes, their martensitic start temperatures are different. Up to date, the cause of such a phenomenon is not clear. Chen *et al.* [13] thought that the defect density in larger particle is larger than that in smaller particle, its nucleation barrier is lower than that of the smaller one. So the M_s of larger particle is higher than that of smaller particles. Evans [14] held that the source of this size effect is the twin phenomenon associated with the transformation. The twins will change the strain energy of the transformation. For different sizes of particles, the degrees of the changes are different. Therefore, the twins will affect the M_s of different particles.

According to Evans' theory [14], we obtain:

$$\frac{2r}{d} = \frac{6\Delta\Gamma_i + 0.13E_p(1+\beta)\gamma_T^2 d}{\Gamma_t + d[\Delta F_0 - 0.28E_p\beta e_T^2/(1+\beta)]} - 2.4 \quad (1)$$

in which, the Poisson's ratio of the matrix and the particles are assumed to be the same, and $\nu_m = \nu_p = 0.2$. r is the radius of the constrained particle. d is the twin space. $\Delta\Gamma_i$ is the surface energy change between the matrix and the particle. Γ_t is the surface energy density between twins. $\beta = E_m/E_p$, E_m and E_p are the Young's moduli of the matrix and the particles, respectively. e_T and γ_T are the volume expansion and the shear deformation associated with the transformation. ΔF_0 is the chemical free energy change and [15]

$$\Delta F_0 = \Delta S(T_0 - M_s) \quad (2)$$

in which ΔS is the entropy change associated with the transformation and T_0 is the temperature at which the t - and m -ZrO₂ have the same free energy. M_s is the martensitic start temperature of the constrained particle.

Generally [14], $\Delta\Gamma_i/E_p\gamma_T^2 d \sim 2 \times 10^{-3}$, $\Gamma_t/d\Delta F_0 \sim 2 \times 10^{-2}$, therefore, we can neglect the $\Delta\Gamma_i$ and Γ_t in Equation 1. Substituting Equation 2 into Equation 1 and neglecting $\Delta\Gamma_i$ and Γ_t , gives:

$$\Delta S[T_0 - M_s(r)] = \frac{0.28E_p e_T^2}{1+\beta} + \frac{0.13E_p(1+\beta)\gamma_T^2}{2.4 + 2r/d} \quad (3)$$

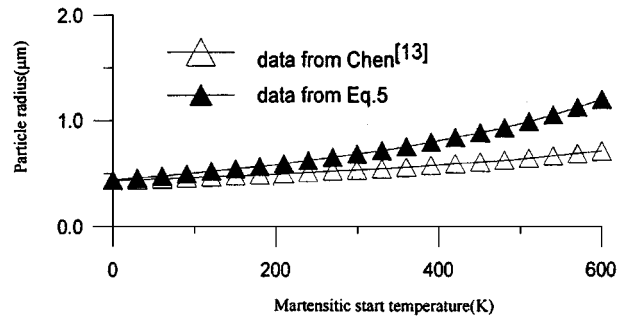


Figure 1 A comparison of Equation 5 to the prediction of Chen.

Let $A = T_0 - \frac{0.28E_p\beta e_T^2}{(1+\beta)\Delta S}$, $B = 1.2d$, $C = \frac{0.13E_p(1+\beta)d\gamma_T^2}{2\Delta S}$, then Equation 3 reduces to:

$$M_s(r) = A - \frac{C}{r+B} \quad (4)$$

Equation 4 shows the relationship between the martensitic start temperature of the constrained t -ZrO₂ particle and its radius r .

In the above analysis, it is supposed that the twin width d is insensitive to the particle size. But in fact, d will slightly increase as r increases. If the particle sizes are in a narrow range of size, it can be deemed that d is a constant for all the transformed particles.

For Al₂O₃/ZrO₂, $E_m = 406$ GPa, $E_p = 204$ GPa, then $\beta \approx 2$. From Garvie [15], we get $T_0 = 1448$ K and $\Delta S \approx 200$ kJ m⁻³ K⁻¹. For the martensitic transformation of a free ZrO₂ particles, $e_T = 0.04$, $\gamma_T = 0.14$. Choosing $d = 0.08$ μm, then $A = 1143$ K, $B = 0.096$, $C = 311$ and thus Equation 4 becomes:

$$M_s = 1143 - \frac{311}{r + 0.096} \quad (5)$$

Fig. 1 is a comparison between Equation 5 and the prediction given by Chen *et al.* [13] based on the experiments of Heuer *et al.* It is shown that Equation 5 shows a good agreement with Chen *et al.* [13] in the interested temperature range (e.g., 0–300 K). In the following parts, Equation 5 will be used to conduct some computations.

3. Particle size distribution

From the experimental observation of Ruhle *et al.* [16], the volume fraction/size distribution of particles in ceramics appears a Gaussian distribution shape. So, to illustrate the effect of the particle size distribution on the properties of the materials, Gaussian distribution for the volume fraction of particles is assumed [17], i.e.,

$$V_f(r) = \frac{V_0}{\sqrt{c'\pi r_0}} \exp\left[-\frac{(r-r_0)^2}{c'r_0}\right] \quad (6)$$

where r is the particle radius, $V_f(r) dr$ is the volume fraction of particles with radius r to $r + dr$, c' is the scale parameter, changing of c' will change the concentration of the distribution. r_0 is the particle radius at which the maximum of $V(r)$ will occur. If it is supposed

that the largest radius of all the transformable t -ZrO₂ particles is r_1 and the smallest is r_s , and $r_1 - r_0 = r_0 - r_s$, then the volume fraction of all the transformable t -ZrO₂ particles is:

$$V_f^0 = \int_{r_s}^{r_1} \frac{V_0}{\sqrt{c'\pi r_0}} \exp\left[-\frac{(r-r_0)^2}{c'r_0}\right] dr \quad (7)$$

Such that:

$$\frac{V_0}{\sqrt{c'\pi r_0}} = V_f^0 / \int_{r_s}^{r_1} \exp\left[-\frac{(r-r_0)^2}{c'r_0}\right] dr \quad (8)$$

4. Transformation toughening

For the materials with an ideal transformation zone in which the volume fraction of the transformed zirconia is uniform, the transformation toughening is given by [18]

$$\Delta K_C = \frac{0.11 E_m e_T (\kappa_m + \kappa_p)}{\kappa_m (1 - \nu_m)} V_f \sqrt{H_0} \quad (9)$$

in which κ_m and κ_p are the volume moduli of the matrix and the particles, respectively. E_m , ν_m are the Young's modulus and Poisson ratio of the matrix. V_f is the volume fraction of the transformed zirconia in the transformation zone and H_0 is the width of the transformation zone. Again, for only a simple analysis, we assume that the Poisson's ratio of the matrix and the particles are the same i.e., $\nu_p = \nu_m$, then Equation 9 becomes:

$$\Delta K_C = \frac{0.11 e_T (E_m + E_p)}{1 - \nu_m} V_f \sqrt{H_0} \quad (10)$$

For the ideally transformed materials, Becher [19] gave out the width of the transformation zone:

$$H_0 = \frac{2(1 + \nu_m)^2}{9\pi} \left(\frac{K_C^m}{\sigma_c^T}\right)^2 \quad (11)$$

where σ_c^T is the critical transformation stress of the constrained particle with certain size. K_C^m is the toughness of the matrix. Substituting Equation 11 into Equation 10, obtains the normalized toughening:

$$\frac{\Delta K_C}{K_C^m} = 0.11 \sqrt{\frac{2}{9\pi}} \frac{e_T (E_m + E_p) (1 + \nu_m)}{(1 - \nu_m) \sigma_c^T} V_f = D V_f \quad (12)$$

in which

$$D = 0.11 \sqrt{\frac{2}{9\pi}} \frac{e_T (E_m + E_p) (1 + \nu_m)}{(1 - \nu_m) \sigma_c^T} \quad (13)$$

According to Becher [8],

$$\sigma_c^T = \Delta S (T - M_s) / e_T \quad (14)$$

Where T is the temperature, M_s is the spontaneous transformation start temperature of the constrained particle.

Substituting Equation 14 into Equation 12, we obtain

$$\frac{\Delta K_C}{K_C^m} = D' \frac{V_f}{T - M_s} \quad (15)$$

in which

$$D' = 0.11 \sqrt{\frac{2}{9\pi}} \frac{e_T^2 (E_m + E_p) (1 + \nu_m)}{(1 - \nu_m) \Delta S} \quad (16)$$

From Equation 15, we could see that when $T \rightarrow M_s$, ΔK_C will go to infinity. But in fact, it is impossible. In literature [8, 10], it is found that as the average particle size of TZP ceramics increases, the width of the transformation zone will increase to a definite value. According to Chen et al. [13], smaller particle has larger nucleation barrier. All these indicate that a minimum stress σ_{\min} maybe exist for stress-induced transformation. Only when the applied stress exceed σ_{\min} , the stress-induced transformation is possible. From Equation 14, for a zirconia particle with radius r , if $\sigma_c^T < \sigma_{\min}$, then $M_s < T < M_s + \sigma_{\min} e_T / \Delta S$, and thus in order to transform the particle, the applied stress must be σ_{\min} .

For transformable materials in which the t -ZrO₂ particles have a size distribution between r_1 and r_s , the spontaneous transformation start temperature M_s and finish temperature M_f [19] exists. From Equation 4, have:

$$M_s = A - \frac{C}{r_1 + B} \quad M_f = A - \frac{C}{r_s + B} \quad (17)$$

Therefore, the temperature range of $T > M_f$ could be divided into four subranges: $T > M_s + \sigma_{\min} e_T / \Delta S$, $M_s < T < M_s + \sigma_{\min} e_T / \Delta S$, $M_f + \sigma_{\min} e_T / \Delta S < T < M_s$, $M_f < T < M_f + \sigma_{\min} e_T / \Delta S$. In the following, the equations of the transformation toughening will be deduced for each subrange.

Case 1: $T > M_s + \sigma_{\min} e_T / \Delta S$. In this case, the critical transformation stress determined by Equation 14 exceeds σ_{\min} for each particle, and the formula of transformation toughening is expressed by Equation 15. The contribution of the particles whose sizes reside in the range of $r \sim r + dr$ to the normalized toughening of the whole materials is:

$$d\left(\frac{\Delta K_C}{K_C^m}\right) = D' \frac{V_f(r)}{T - M_s(r)} dr \quad (18)$$

When $T > M_s + \sigma_{\min} e_T / \Delta S$, it is assumed that all the t -ZrO₂ particles can be transformed to m -ZrO₂ by the applied stress. Then the normalized toughness increment of the whole material is:

$$\begin{aligned} \frac{\Delta K_C}{K_C^m} &= D' \frac{V_0}{\sqrt{c'\pi r_0}} \int_{r_s}^{r_1} \frac{1}{T - A + C/(r + B)} \\ &\times \exp\left[-\frac{(r-r_0)^2}{c'r_0}\right] dr \end{aligned} \quad (19)$$

Case 2: $M_s < T < M_s + \sigma_{\min} e_T / \Delta S$. In this case, a critical radius r_{c1} exists. All the t -ZrO₂ particles whose

radii are larger than r_{c1} will be transformed under the minimum stress σ_{\min} .

Let

$$\sigma_c^T = \Delta S[T - M_s(r_{c1})]/e_T = \sigma_{\min} \quad (20)$$

then

$$r_{c1} = \frac{C}{A - T + \sigma_{\min}e_T/\Delta S} - B \quad (21)$$

The contribution of the particles with radii between r_1 and r_{c1} to the normalized toughening is:

$$\frac{\Delta K_{1C}}{K_C^m} = D \int_{r_{c1}}^{r_1} V_f(r) dr \quad (22)$$

where σ_c^T should be substituted by σ_{\min} in Equation 13. The contribution of the particles with radii between r_s and r_{c1} is:

$$\frac{\Delta K_{2C}}{K_C^m} = D' \int_{r_s}^{r_{c1}} \frac{V_f(r)}{T - M_s(r)} dr \quad (23)$$

Therefore, the stress-induced transformation toughening of the whole materials is:

$$\frac{\Delta K_C}{K_C^m} = \frac{\Delta K_{1C}}{K_C^m} + \frac{\Delta K_{2C}}{K_C^m} \quad (24)$$

Case 3: $M_f + \sigma_{\min}e_T/\Delta S < T < M_s$. In this case, spontaneously transformation occurs, and a critical radius r_{c2} exists. Particles with a radius larger than r_{c2} would spontaneously transform to their monoclinic phase. Let $M_s = T$ and $M_s = T - \sigma_{\min}e_T/\Delta S$, then:

$$r_{c2} = \frac{C}{A - T_s} - B \quad (25)$$

$$r_{c3} = \frac{C}{A - T + \sigma_{\min}e_T/\Delta S} \quad (25')$$

From Equation 12, the particles with radii between r_{c2} and r_{c3} will be transformed under the minimum stress σ_{\min} . Their contribution to the toughening is:

$$\frac{\Delta K_{1C}}{K_C^m} = D \int_{r_{c3}}^{r_{c2}} V_f(r) dr \quad (26)$$

where σ_c^T should be substituted by σ_{\min} in Equation 13. From Equation 14, the contribution of the particles with radii between r_s and r_{c3} is:

$$\frac{\Delta K_{2C}}{K_C^m} = D' \int_{r_s}^{r_{c3}} \frac{V_f(r)}{T - M_s(r)} dr \quad (27)$$

Then, the normalized toughening of the whole materials is:

$$\frac{\Delta K_C}{K_C^m} = \frac{\Delta K_{1C}}{K_C^m} + \frac{\Delta K_{2C}}{K_C^m} \quad (28)$$

Case 4: $M_f < T < M_f + \sigma_{\min}e_T/\Delta S$. In this case, all the remaining particles with radii residing in the range of $r_s \sim r_{c2}$ will be transformed by the minimum stress

σ_{\min} . The contribution of these particles to the toughening of the materials is:

$$\frac{\Delta K_C}{K_C^m} = D \int_{r_s}^{r_{c2}} V(r) dr \quad (29)$$

Where σ_c^T should be substituted by σ_{\min} in Equation 13.

5. Examining of examples and discussions

We choose Al_2O_3 -20%vol. ZrO_2 as the examining object. For $\text{Al}_2\text{O}_3/\text{ZrO}_2$, $E_m = 406$ GPa, $E_p = 204$ GPa, $e_T = 0.04$, $\gamma_T = 0.14$, and $\Delta S \approx 200$ $\text{kJ m}^{-3} \text{K}^{-1}$, $V_f^0 = 0.2$. Chen [20] and Hannink [21] have studied the relationship between the critical transformation stress of Ce-TZP and the temperature. From their data, we obtain $\sigma_{\min} = 20$ MPa, then $\sigma_{\min}e_T/\Delta S = 4$ K.

From Section 3, it could be seen that if r_1 , r_s , c' change, $V_f^0 = \int_{r_s}^{r_1} V_f(r) dr$ will change, and so does the transformation toughening. The following is some results and discussions with changing of r_1 , r_s , and c' .

5.1. Transformation toughening and temperature

The curves in Fig. 2 is got by choosing $r_1 = 0.28$ μm , $r_s = 0.18$ μm , $c' = 0.01r_0$. From curve 1 in Fig. 2, it could be seen that as the temperature decreases, the toughness of the materials increase at first, then decreases with decreasing of temperature after reaching a certain temperature. The temperature (T_{\max}) at which the toughness reach its maximum value is only a little above $M_s(r_0)$. The cause of such a phenomenon is the size distribution of the zirconia particles in the material. For such materials, if r_f is not small enough and $M_s(r_s) > 0$ K, then when the temperature drops from a high value, the materials will exhibit a macro martensitic start temperature M_s and a macro martensitic finish temperature M_f . When T drops but T is still above M_s , from Equation 14, the critical transformation stress of all the zirconia particles will decrease and the width of the transformation zone will increase, and then the toughness of the materials will increase with decreasing of temperature. When T drops below

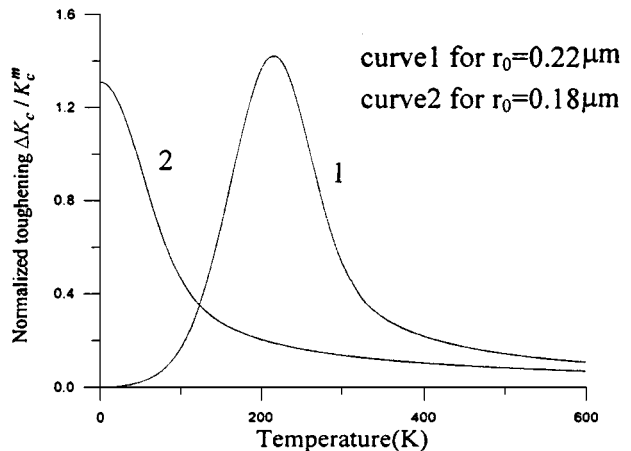


Figure 2 Relations of normalized toughening and temperatures.

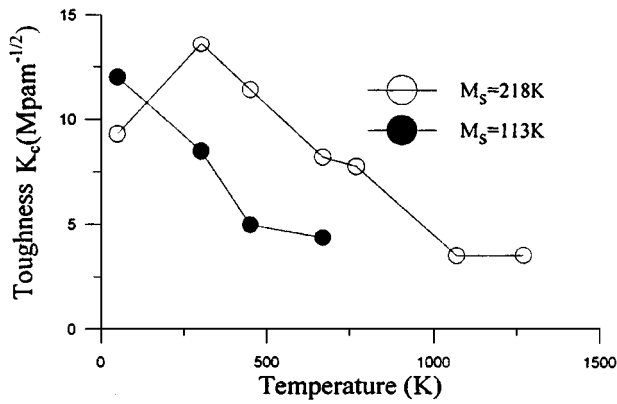


Figure 3 Relationships between toughness and temperatures for MgO-PSZ from data of [19].

M_s , the spontaneous transformation will happen, and the volume fraction of the stress induced transformable particles will decrease. On the other hand, decreasing of T will decrease the critical transformation stress of the untransformed zirconia particles, then increase the toughness. These two factors combine to contribute to the toughening of the materials and the toughness of the materials could also increase while T is below M_s . As stated previously, r_0 is the particle radius which gives the maximum of $V(r)$. So, if T drops below $M_s(r_0)$, most of the zirconia particles in the materials have transformed spontaneously. The increase of toughening caused by the drop of T can not offset the decrease of toughening caused by loss of transformable zirconia particles. Thus the toughness of the materials will drop. When $T < M_f$, all the zirconia particles have been transformed and there will be no stress-induced transformation. But the transformed particles will result in a residual stress distribution in the materials. The residual stress will deflect the main crack [22] or result in the microcracks [23] under applied stress, and thus will also increase the toughness of the materials. But this kind of toughening is not discussed here.

From the analysis above and the curve 2 in Fig. 2, it could be seen that if the radii of the particles are small enough to make T_{max} nearly 0 K, then the toughness of the materials would always increase as T drops as shown by curve in Fig. 2. Therefore, if we want to get materials with the high toughness at low temperatures, it is needed only to make the sizes of the particles small enough by heat treatment.

The curves in Fig. 3 are gotten from Becher [19] for MgO-PSZ. Although the composition of MgO-PSZ and that of Al_2O_3/ZrO_2 is different from each other, there is similar particle size effect in these materials [19] and the mechanism of transformation toughening in these two systems are really the same. It is shown that the relationships between toughness and the temperature shown in Fig. 3 are similar to the relationship predicted in Fig. 2, thus justifies the previous analysis.

5.2. Effect of the range of zirconia size distribution on the toughness

Let r_0, c' be constant and changing $r_1 - r_s$, then the curves are given in Fig. 4. It is seen that if r_0 is a con-

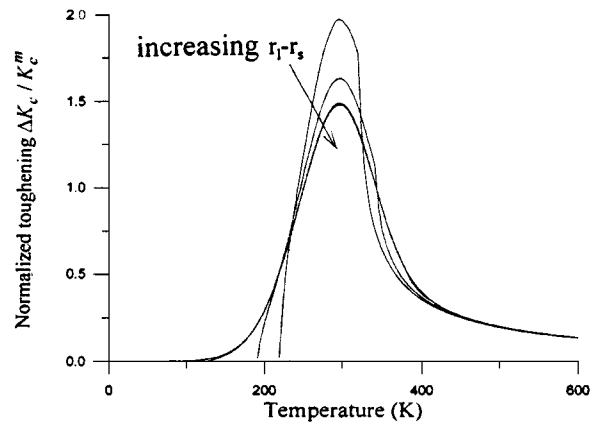


Figure 4 Curves of normalized toughening to temperature with increasing $(r_1 - r_s)$ for $r_0 = 0.3 \mu m, c' = 0.01r_0$.

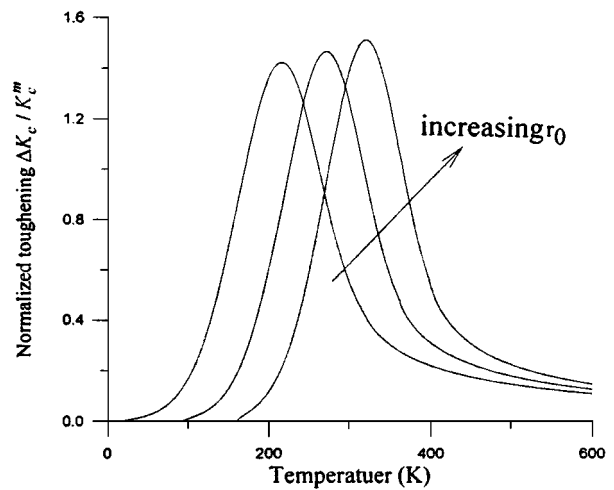


Figure 5 Curves of normalized toughening to temperature with increasing r_0 for $r_1 - r_s = 0.1 \mu m, c' = 0.01r_0$.

stant, then the temperature (T_{max}) at which the toughening of the materials reach its maximum will not change with increasing of $(r_1 - r_s)$. The maximum normalized toughening $(\Delta K_c)_{max}/K_c^m$ of the materials decreases as $r_1 - r_s$ increases. On the other hand, the maximum toughness of the materials and T_{max} increase with increasing of the average particle size r_0 , for a given $r_s - r_f$, as shown in Fig. 5, all these indicate that r_0 determines the maximum toughening of the materials and T_{max} . It is a possible reason that most of the zirconia particles concentrate around r_0 for Gaussian distribution, and the toughening of the materials are mainly determined by the stress-induced transformation of these particles. Fig. 6 gives out the relationship between r_0 and $(\Delta K_c)_{max}/K_c^m$. It is shown that $(\Delta K_c)_{max}/K_c^m$ increases as r_0 increases and the curve is approximately linear. Fig. 7 indicates that $(\Delta K_c)_{max}/K_c^m$ will decrease if $r_s - r_f$ increases, but when $r_s - r_f$ becomes larger, $(\Delta K_c)_{max}/K_c^m$ will reach a definite value. The reason of such a phenomenon is that larger $r_s - r_f$ decreases the volume fraction of the zirconia particles concentrating around r_0 , thus make $(\Delta K_c)_{max}/K_c^m$ drop.

Fig. 8 is the relationship between the toughening and r_0 at 300 K. It shows that $(\Delta K_c)_{max}/K_c^m$ increases first with the increase of r_0 and then drops rapidly after reaching a maximum of $(\Delta K_c)_{max}/K_c^m$. Fig. 9 is the

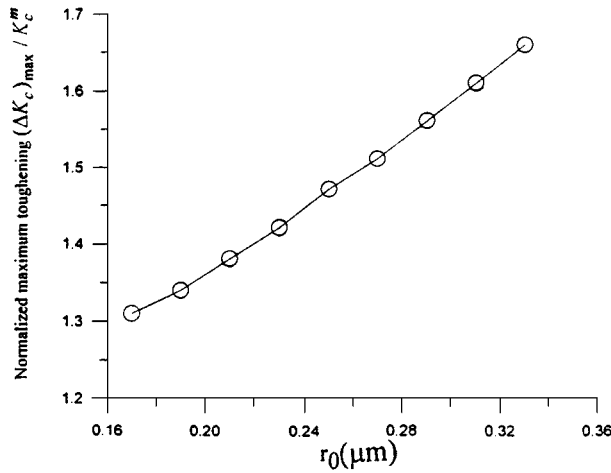


Figure 6 Relation between the normalized maximum toughening and the average particle size r_0 for $r_1 - r_s = 0.1 \mu\text{m}$, $c' = 0.01r_0$.

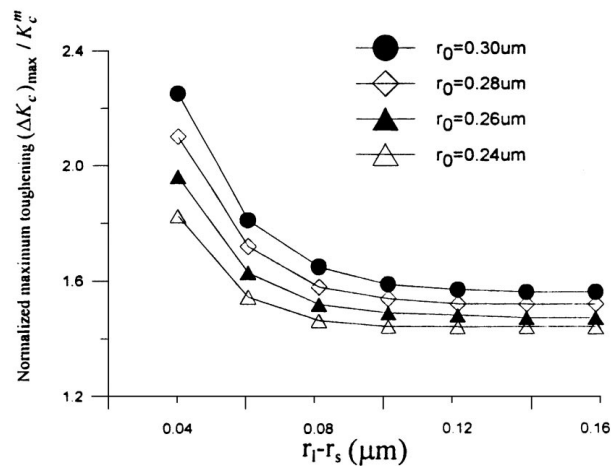


Figure 7 Curves of normalized maximum toughening to $r_1 - r_s$ with different r_0 for $c' = 0.01r_0$.

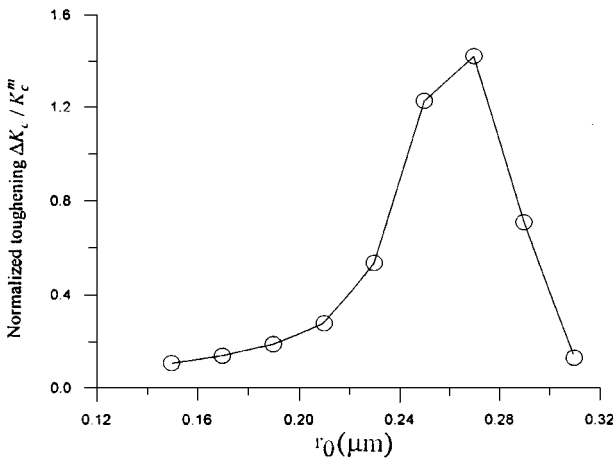


Figure 8 Relation between the normalized toughening and r_0 at 300 K for $r_1 - r_s = 0.1 \mu\text{m}$, $c' = 0.01r_0$.

experimental data from other workers [24] for Y-TZP. It is found that their curves are similar to the curve in Fig. 8. At room temperature, if we increase the zirconia particle sizes, the martensitic start temperature M_s of the particles will increase toward room temperature. If $M_s(r)$ is larger than room temperature, the spontaneous

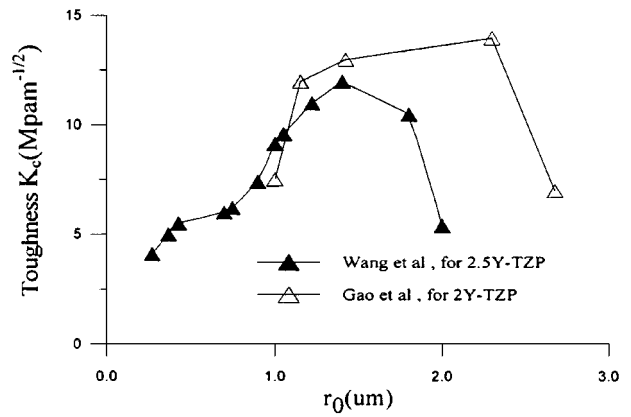


Figure 9 Relation between the toughness and r_0 at 300 K from other workers' experiments.

transformation will easily occur, thus will diminish the volume fraction of the transformable zirconia particles. So, the toughness of the materials will decrease.

5.3. Effect of size distribution shape on the toughness

Fig. 10 gives out $(\Delta K_c)/K_c^m \sim T$ curves for different c' . When c' increase, the $(\Delta K_c)_{\text{max}}/K_c^m$ drops and T_{max} increases, but the range of temperature in which the toughness of the materials is larger than certain value becomes wider. When c' is very large, the $(\Delta K_c)/K_c^m \sim T$ curves are almost the same as shown by the curve for $c' = 0.81r_0 \sim 10r_0$ in Fig. 10 and the toughening of the materials is higher at a wider range of temperature.

For Gaussian distribution, variation of c' will change the shape of the distribution. Increasing of c' will make the distribution of volume fraction/size become less concentrated in the range of $r_s < r < r_1$, thus will diminish the volume fraction of zirconia with radius around r_0 . When T drops from a value lower than M_s to a definite value, the volume fraction of the spontaneously transformed zirconia in the materials with larger c' will be larger than that of the materials with smaller c' , and the volume fraction of the stress-induced transformed

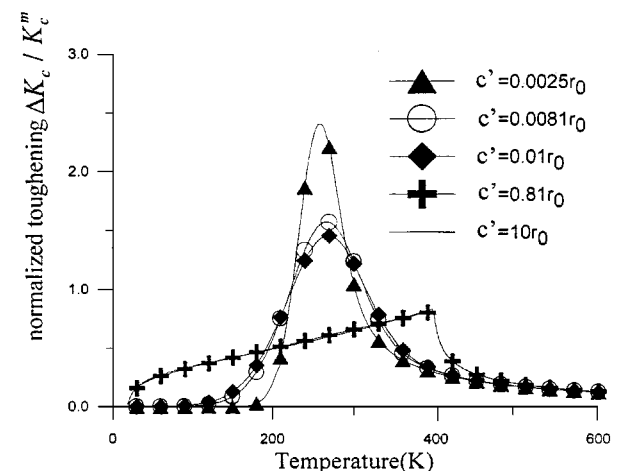


Figure 10 Effect of c' on the curves of normalized toughening to temperature with different c' for $r_1 = 0.34 \mu\text{m}$, $r_s = 0.20 \mu\text{m}$, $r_0 = 0.27 \mu\text{m}$.

zirconia in the former materials will become smaller than that in the latter materials. So, $(\Delta K_c)_{\max}/K_c^m$ drops as c' increases.

6. Conclusions

(1) For ZrO₂-containing ceramics, if the particles are not fine enough, when the temperatures drops, the toughness of the material will increase at first, and then decrease to a certain value slightly larger than the toughness of the matrix, after reaching a maximum toughness. If the zirconia particles become finer, the $(\Delta K_c)_{\max}/K_c^m \sim T$ curve will move toward the lower temperature range. Therefore, if we want to get materials with high toughness at cryogenic temperatures, we need only to make the zirconia particles in the materials fine enough.

(2) The maximum toughening $(\Delta K_c)_{\max}$ of the materials is approximately linear to the average particle size (r_0) and increase with increasing r_0 . The temperature at which the toughening reaches its largest value will also increase with increasing r_0 . When r_0 increases, the toughening of the material at given temperature will increase at first, then drops after reaching a maximum value.

(3) The more concentrated the distribution of volume fraction/size, the higher $(\Delta K_c)_{\max}$ will be. If the distribution becomes less concentrated (either $r_s - r_f$ or c' increases), $(\Delta K_c)_{\max}$ will decrease but the range of temperature in which the toughening is larger than a certain value will become wider. If $r_1 - r_s$ or c' becomes large enough, $(\Delta K_c)_{\max}$ will reach a definite value.

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