MICROSTRUCTURAL TAILORING OF TRANSFORMATION TOUGHENED CERAMICS

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ABSTRACT

The tetragonal-to-monoclinic transformation temperature M_S and the transformation toughening contribution ΔK^T increase with increase in grain size of the tetragonal zirconia present in either polycrystalline tetragonal zirconia or zirconia-toughened alumina composites. However, the grain size dependence of both M_s and ΔK^T increases with decrease in zirconia content. Thus, the microstructures of such materials must be carefully tailored to optimize their performance. This has been achieved here by employing colloidal processing conditions which promote weak particle-particle interactions in the binary suspension to obtain uniform spatial distribution of both the zirconia and alumina phases and to maintain the initial narrow size distributions by minimizing agglomeration and differential settling. Sintering conditions were then utilized to obtain dense materials of selected grain sizes. However, the grain growth rates are influenced by the degree of interconnectivity of the phases. For example, decreasing the zirconia content results in reducing the zirconia grain growth rates.

Theoretical analysis reveals that the main factor in the grain size dependency of the transformation behavior is the increasing contribution of internal residual tensile stresses, generated by thermal expansion anisotropy/mismatch, with increase in grain size. The observed increase in the dependence of M_S on grain size for Al_2O_3-ZrO_2 (12 mol % CeO_2) composites with increasing alumina content vs that for ZrO_2 (12 mol % CeO_2) ceramics confirm the role of the internal residual stress contribution in promoting the transformation. The control of the M_S temperature by

regulating the zirconia grain size then allows the fracture toughness of each the composites to be optimized.

INTRODUCTION

There has been considerable success in utilizing the stress-induced martensitic transformation of tetragonal zirconia to increase the fracture resistance/toughness of both partially stabilized zirconias PSZ, and polycrystalline tetragonal zirconias TZP.[1-10] Room temperature fracture toughness values of 10 to 20 MPa m$^{1/2}$ can be achieved; however, the thermodynamic character of this transformation results in a decrease in toughness with increase in test temperature.[8] There has also been some success in toughening other ceramic matrices via the addition of zirconia grains/particles (e.g., the zirconia-toughened ceramics, ZTC). The results achieved with ZTC materials are, however, quite variable, even when employing the same matrix, zirconia content, and solute addition to zirconia.[2b,3,9,10] This can be attributed to various degrees of toughening contributed by the stress-induced transformation and by microcracking in ZTC due to differences in zirconia grain size and distribution.

The transformation toughening contribution can be shown to depend on the difference between the test temperature T and the M_S temperature where $T > M_S$.[4,7,8a] The stress-induced transformation component of the toughness is:

$$\Delta K^{T'} \approx \left[E V^T B/(1 - \nu^2)\Delta S^{t\to m}(M_s - T)\right]^{1/2}(K_I \epsilon^T), \tag{1}$$

where $\Delta K^{T'}$ designates the value is dependent upon the magnitude of the applied stress intensity K_I, V^T is the volume fraction of tetragonal phase that transforms, ϵ^T is the volumetric transformation strain (4 to 5%), B equals $[3^{1/2}(1 + \nu)^2/12\pi]$ with ν being the Poisson's ratio, $\Delta S^{t\to m}$ is the entropy change of the tetragonal-to-monoclinic (t-to-m) transformation (negative value), and E is the Young's modulus of the system.[7] The ΔK^T values for crack propagation can be obtained by substituting K_o, the matrix fracture toughness in the absence of transformation toughening into Eq. (1) for K_I.[7] The end result is that the transformation toughening contribution, ΔK^T, is sensitive to material characteristics, the martensite start temperature M_S, and the test temperature T.

It is well known that both the amount and type of solute used to retain the tetragonal phase at room temperature influence the room temperature toughness of TZP ceramics. Small increases in yttria content can dramatically reduce the fracture toughness at room temperature as the martensitic t-to-m transformation temperature M_S is depressed several hundred degrees within the t/m phase field (e.g., 0 to 2.5 mol % yttria).[1] Ceria, however, has a much weaker effect on depressing M_S as the t/m phase field is nearly 10-fold larger (i.e., extending from 0 to 18–20 mol %).[11] Because of the narrow tetragonal phase field, variations in solute content can be a significant factor in the variation of fracture toughness values obtained for TZP and ZTC materials employing zirconia-yttria alloys.

As seen earlier in PSZ ceramics of the same chemical composition and containing tetragonal precipitates, the room temperature toughness values increase with increase in the size of the metastable tetragonal precipitates.[8a] Similar toughness increases with increase in tetragonal phase grain size have been demonstrated in TZP ceramics employing yttria[5] and ceria[7] solutes. This grain size dependent toughening is associated with the increase in the martensite start temperature which increases with the size of the tetragonal phase precipitates and grains.[7,8a] Thus, the transformation toughening behavior can again be expressed by Eq. (1) after accounting for the grain size dependence of the M_S temperature.

Several mechanisms have been proposed to be the source of this grain size dependent transformation behavior including those related to nucleation,[12,13] surface energy,[2a,14] and internal residual stress.[15,16] In the present work, we will show that the M_S-grain size relationship can be primarily derived from the internal tensile stresses, σ_{TEA} (e.g., due to thermal expansion anisotropy or mismatch), acting as part of the driving force to initiate the transformation.[7] Such σ_{TEA} stresses can result from the large anisotropy in crystallographic thermal expansion coefficients ($\Delta\alpha$) that exist in the pure tetragonal phase (but which decrease as the solute content increases[16]). Mismatch in expansion coefficients between the matrix and the zirconia is another source of these internal stresses. During cooling over a temperature range, ΔT, from an elevated temperature where the stresses are frozen-in (T_{SR}) to, for example, room temperature, the anisotropy and lattice misorientations across grain boundaries combine to introduce local internal stresses (e.g., $\sigma_{TEA} = E\Delta\alpha\Delta T$) at grain boundaries. Analytical solutions reveal that these stresses exhibit concentration profiles near grain corners and edges which take the form $\sigma_i = \sigma_{TEA}\, d/r$, where d is the size of the grain and r is the distance from the stress concentrating feature.[17,18] Combining these factors, one can show that:

$$M_s = M_s^o - \left[\epsilon^T / \Delta S^{t\to m} r_{crit}\right](E\Delta\alpha\Delta T d), \qquad (2)$$

where M_S^o is the transformation temperature in the absence of internal stresses and r_{crit} is the critical size necessary to trigger transformation. Because the value of $\Delta S^{t\to m}$ is negative, Eq. (2) indicates that the M_S temperature increases with increase in grain size and that this dependence is modified by changes in the E and $\Delta\alpha$ terms.[7] This, then, provides a basis for the grain size dependence of the M_S temperatures and the dependence of the transformation toughening contribution on M_S observed in PSZ[8a] and TZP.[5,7]

One would also expect that in composites containing a mixture of zirconia and matrix grains that microstructural control is important in optimizing the fracture toughness. Indeed, it is the lack of control of the particle size distributions of the zirconia and matrix powders and the uniformity of mixing during powder processing, coupled with failure to control grain growth during sintering, that are the critical aspects in the variable toughening results in ZTC composites. As shown in our prior studies, the size and spatial distribution of zirconia grains within a ceramic matrix (e.g., alumina) can be regulated by employing systematic colloidal processing and sintering approaches.[19] The present paper illustrates the role of processing to control grain size and spatial distributions, the M_S temperatures, and, in turn, the tailoring of the room temperature fracture toughness of alumina-zirconia (12 mol % ceria) composites and TZP ceramics containing 12 mol % ceria.

DISCUSSION

Microstructural Tailoring

We have focused on colloidal processing to control the microstructure of alumina-zirconia specifically to (1) control the particle size distributions of the alumina and zirconia powders and (2) ensure uniform mixing of the alumina and zirconia and high green state densities while avoiding reagglomeration and differential settling of the two powders. Details of these processing experiments and the fundamental aspects are described in depth elsewhere,[19] and are only briefly described here. Each powder was dispersed separately in an aqueous HCl solution (pH 3 to 4) containing 0.01 mol NaCl/L; sonicated suspensions were allowed to stand briefly so that large particles could settle. The fine particles remaining in suspension were then separated by decantation to obtain narrow size distributions of each powder. Concentrated, intimately mixed binary slurries were produced typically at pH values of 5.5 ± 0.1, which is below the isoelectric points of both the zirconia and the alumina. From studies of suspension settling and rheological behavior, it was determined that such conditions produced alumina-CeTZP-water suspensions that allow for weak particle-particle interactions and optimum particle packing in the consolidated (e.g., by pressure filtration) samples. Furthermore, control of both the mean powder particle sizes by fractionation and the ratio of the mean size of the zirconia powder to that of alumina minimized differential settling of the denser zirconia powder.

Green pieces of alumina containing 20 and 40 vol % zirconia (12 mol % ceria) were formed by pressure filtration and, then, dried. The dried green pieces typically exhibited densities exceeding 55% of theoretical density (water immersion of paraffin-coated samples). Sintering in flowing oxygen at 1500°C for 1 h was sufficient to achieve >98% of theoretical density; 1650°C sintering conditions were used to promote grain growth in order to examine zirconia grain size effects on the transformation behavior. The success of our colloidal processing approach is indicated by the uniform spatial distribution of the zirconia and alumina grains in sintered ZTA composites, as shown in Fig. 1a. The advantages of using size-fractionated powders can be readily discerned by comparing the micrographs of the size-fractionated and as-received powders, Figs. 1a and 1b respectively. Comparison of Figs. 1a and 1c shows that a slight increase in pH from 5.4 to 6.1 has an effect on the resultant composite microstructure and density.[19]

The zirconia grain size distribution and the mean grain size of the ZTA composites sintered at 1500°C for 1 h is similar to those of the initial fractionated powder. Grain growth was achieved by increasing the sintering time at 1500 and 1650°C as shown in Fig. 1d. The extent of grain growth as a function of time, however, is influenced by the zirconia content as seen in earlier studies.[20] The influence of zirconia content is reflected by the grain growth rate constant K where $G^3 - G_o^3 = Kt$, the grain size is G at time t, and G_o at to. Here to is taken as the minimum time to obtain full density at a given sintering temperature. The K values associated with growth of the zirconia grains decrease with decrease in zirconia content asymptotically approaching a lower limit at ZrO_2 contents <20 vol % as seen in Fig. 2. Similar behavior is seen for the growth of alumina grains with decrease in alumina content. The rapid increase in the growth rates of ZrO_2 grains as the zirconia content is raised above ~20 vol % is a result of the formation of an interconnected zirconia structure which decreases the diffusion path and alters the dihedral angles (e.g., ZrO_2-ZrO_2-Al_2O_3 vs Al_2O_3-Al_2O_3-ZrO_2 grain junctions) and the grain coordination number.[20b] The volume content at which the second phase grains start to become interconnected can be determined from percolation theory. Typically, random ordering of the second phase is assumed, and particles of equal size become interconnected at ~15 vol %; however, decreasing the randomness of the ordering requires increasing second phase content to establish connectivity of the phase.

The result is that uniform microstructures with controlled tetragonal ZrO_2 grain sizes can be developed by giving attention to the colloidal behavior of binary suspensions. Specifically the use of powders with narrow size distributions and size ratios and processing conditions which promote weak particle interactions while avoiding agglomeration are of primary concern. This approach allows one to produce green state microstructures with the desired intimate mixing of the alumina and zirconia phases and the narrow size distribution of each phase, while achieving high green state densities. Tailoring the green state microstructure to achieve the desired microstructure is required to obtain dense sintered composites with the desired transformation characteristics and toughening behavior. Use can then be made of the sintering conditions to tailor the grain size (Fig. 1d); however, one must account for the effect of second phase content and interconnectivity on grain growth rates. Therefore, lower zirconia content ZTA composites require longer times to achieve grain sizes equivalent to those of higher zirconia content ZTA composites. This can be a critical aspect in employing processing/densification conditions to tailor the transformation behavior and toughness of the dense composites.

Transformation Behavior

Based on the scaling of the internal residual stresses with increase in grain size predicted by Eq. (2), the martensite start temperature, M_S, for the tetragonal-to-monoclinic transformation should rise linearly with increase in zirconia grain size. In addition, the rate of rise in M_S temperature with increase in grain size must increase with increase in the Young's modulus and mismatch in the thermal expansion coefficients, $\Delta\alpha$, if the internal residual stress effect is significant. Each of these features is reflected in the experimental results shown in Fig. 3 for both the ZTA with 20 and 40 vol % ZrO_2 (12 mol % CeO_2) and the polycrystalline tetragonal ZrO_2 (12 mol % CeO_2). The grain size effect is quite obvious and becomes stronger as alumina is added.

The more rapid rise in M_S, as grain size increases with increasing alumina content, is a result, in part, of the increase in Young's modulus [i.e., E is 400 and 190 GPa for alumina and ZrO_2 (12 mol % CeO_2), respectively]. In addition, the value of $\Delta\alpha$ in Eq. (2) increases as alumina is added. The value of $\Delta\alpha$ is simply the difference of the thermal expansion coefficients in the c- and a-axis directions for ZrO_2 (12 mol % CeO_2) ceramics (i.e., roughly 2 x 10^{-6}/°C accounting for the ceria content). On the other hand, the mismatch in the mean thermal expansion coefficients of alumina and ZrO_2 (12 mol % CeO_2) yields a $\Delta\alpha$ value of $\sim 5 \times 10^{-6}$/°C. Thus, both E and $\Delta\alpha$ increase with the addition of alumina which would then account for the increase in slope of the M_S-vs-grain size plots as predicted by Eq. (2). Therefore, the experimental results emphasize the important role that internal residual tensile stresses play in the martensitic transformation of zirconia.

The above results are based on a fixed solute content (12 mol % ceria) in the zirconia. Earlier studies of the yttria-zirconia TZP system show that $\Delta\alpha$ is decreased by increasing the yttria content. This has the effect of reducing the internal residual tensile stress for a given grain size, and, thus, requires a much greater applied stress to transform the tetragonal phase as more yttria (or other stabilizing solute) is added.[16] This is consistent with a variety of observations[1,2,4,5,9a,16] and further confirms the substantial contribution of internal residual stress mechanisms to the transformation of tetragonal zirconia ceramics and composites.

Based on the transformation toughening behavior predicted by Eq. (1) and the ability to control the tetragonal-to-monoclinic transformation temperature through the zirconia grain size, one should be able to control the fracture toughness in the same manner. Experimental results reveal that the room temperature fracture toughness of these same ZTA composites and the TZP ceramics increases as the M_S temperature is raised and approaches 22°C, Fig. 4. Therefore, growth of the zirconia grains can be used to enhance the transformation toughening contribution. Note there is an upper limit to the zirconia grain size that can be exploited, as Eq. (2) predicts that the grains will spontaneously transform while cooling to room temperature from the sintering temperature when d is greater than a critical grain size (i.e., $M_s > 20°C$). This will result in a loss of tetragonal phase that is available to contribute to transformation toughening [e.g., V^T in Eq. (1) will decrease].

The combination of the amount of tetragonal zirconia present V_{Zr} and the fraction f of the tetragonal phase present which transforms (i.e., $V^T = f\,V_{Zr}$) is an important factor in determining the slope of the fracture toughness plot for each material illustrated in Fig. 4. From X-ray measurements, the zirconia in each material is initially present solely as the tetragonal phase. In the absence of measurements of the monoclinic contents of the fracture surfaces, we can illustrate the trend in the amount of tetragonal phase which transforms V^T from the liquid nitrogen dilatometry transformation hysteresis data. These results indicate that the amount V^T of transformed ZrO_2 increases with increasing zirconia content, but the fraction f remains nearly constant. Thus, the increase in V^T is the major factor for the increase in the slope of the 40 vol % vs 20 vol % zirconia (12 mol % ceria) composite results in Fig. 4 as the V^T term in Eq. (1) increases with increase in tetragonal zirconia content.

Based on the increase in V^T with increase in zirconia content, one would expect that the slope for the CeTZP ceramics would be greater than that of either of the composites. However, the slope is also directly dependent upon the E value which for the CeTZP ceramics is much lower (~1/2) than that of the composites. Note that the effects on the slope due to the differences in E value for the two composites is much smaller and are overshadowed by the large differences in V^T. The key point is that by controlling the zirconia grain size in the alumina-zirconia composites, the M_s temperature can be systematically raised resulting in a large transformation toughening contribution rivaling that achieved in the TZP ceramics.

CONCLUSIONS

The transformation toughening contribution to the fracture resistance of polycrystalline tetragonal zirconias and ceramic composites containing tetragonal zirconia grains can be optimized by microstructural tailoring. This involves the use of colloidal processing to select the desired particle size distributions, to prevent agglomeration of the powders, and to obtain uniform mixing of the two phases. The present study reveals that zirconia-toughened alumina composites with very fine grain sizes and narrow size distributions, in which the zirconia phase is uniformly distributed throughout the alumina matrix, can be developed by proper attention to each processing step. In fact, with well-controlled processing, the grain size distributions in composites sintered at 1500°C for 1 h are similar to those of the as-fractionated powders. Grain growth rate constants K for both the zirconia and alumina phases vary significantly with zirconia content; the K value for zirconia decreases from being essentially equal to that of alumina to $\sim 1/5$ that of alumina as the zirconia content decreases from 40 to 20 vol %. This is a result of the loss of interconnectivity of the zirconia phase and the change in dihedral angle with increase in alumina neighbors as the zirconia level decreases. Such compositional effects on the grain growth responses must be considered in the densification of zirconia toughened ceramics to obtain the microstructural characteristics desired.

This is a critical point because the tetragonal-to-monoclinic transformation M_S temperature for both Al_2O_3-ZrO_2 (12 mol % CeO_2) composites and ZrO_2 (12 mol % CeO_2) ceramics increases with increase in ZrO_2 grain size. A major factor is the increasing contribution of the internal residual tensile stresses due to thermal expansion anisotropy/mismatch with increase in grain size. Analysis of the internal residual stress contribution reveals that the grain size dependence of M_S should increase with increasing Young's modulus and thermal expansion mismatch which is supported experimentally. Thus, the addition of alumina increases both E and $\Delta\alpha$ and results in a much greater sensitivity of M_S to changes in the zirconia grain size. The significance of these findings is that the transformation toughening contribution increases as the difference between the M_S and test temperature, T, decreases when $T > M_S$. This is supported by both the theoretical and experimental results. Therefore, increasing the zirconia grain size is an effective means of optimizing the fracture toughness of ZTC and TZP material. However, variations in the tetragonal zirconia grain size and broad size distributions are two common sources of scatter in the fracture resistance achieved by transformation toughening.

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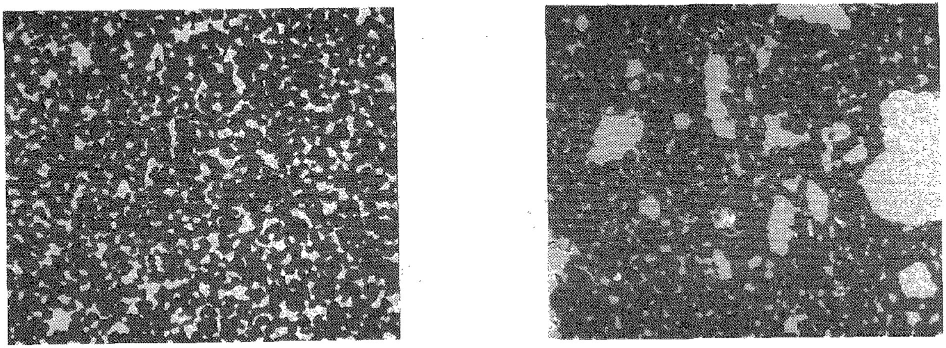
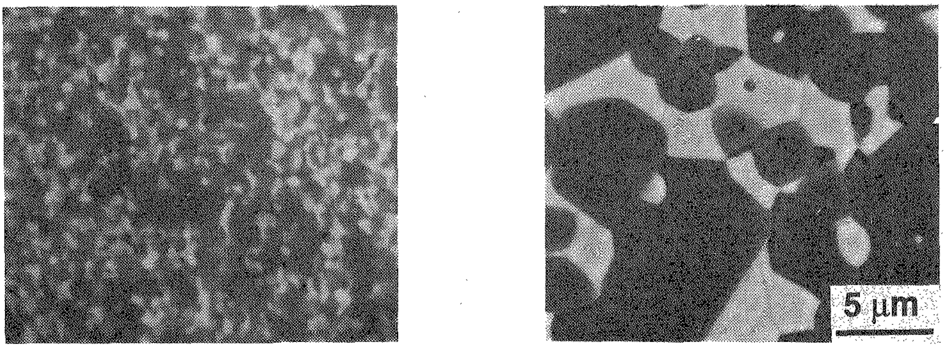


(a) $\rho_g = 0.61$ $\rho_s = 1.00$

(b)



(c) $\rho_g = 0.55$ $\rho_s = 0.94$

(d)

Fig. 1. Microstructures of Al_2O_3-20 vol % ZrO_2 (12 mol % CeO_2) composites colloidally processed and sintered under differing conditions. The green density, ρ_g, and the sintered density, ρ_s, are shown for (a) and (c). Dense sintered (1500°C, 1 h) specimen colloidally processed at pH 5.5 fabricated from (a) fractionated powders and (b) as-received powders. (c) Specimen processed and sintered similar to (a) except a pH of 6.1 was used. (d) Grain growth resulting from an increase in both sintering time and temperature (1650°C, 45 h).

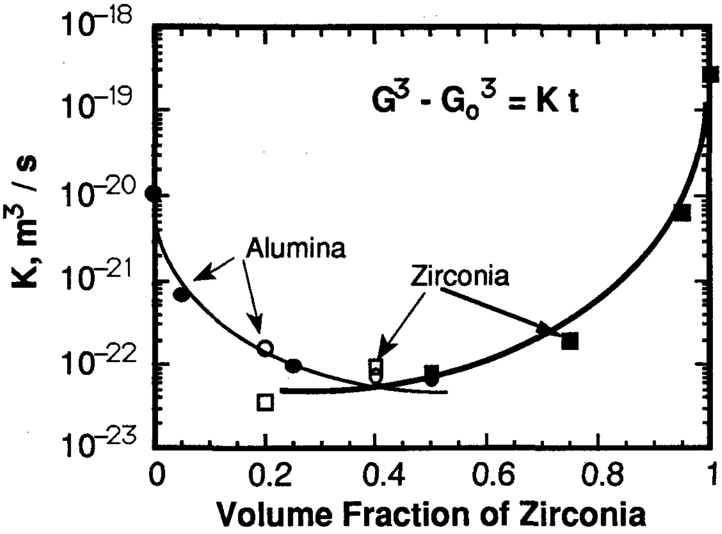


Fig. 2. The grain growth rate constant K for ZrO_2 grains increases with increase in ZrO_2 content. Zirconia grain growth represented by squares and that for alumina by circles; data represented by closed symbols are from Ref. 20a.

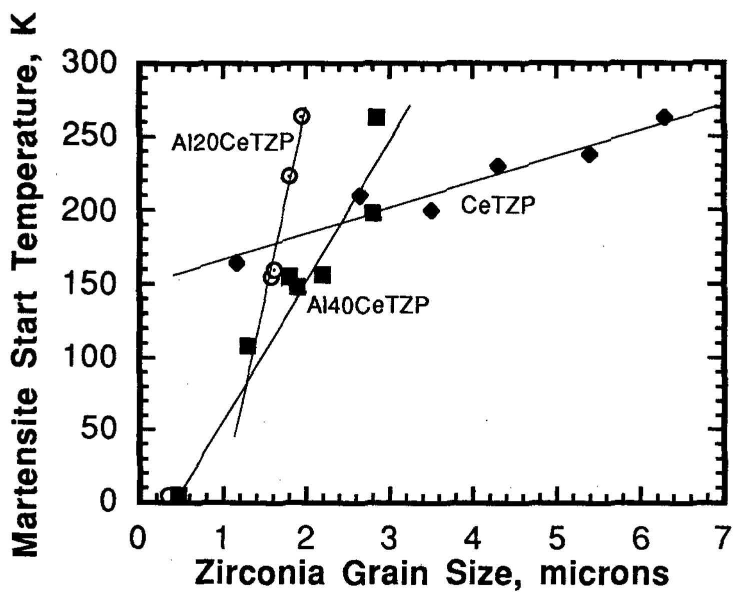


Fig. 3. The tetragonal-to-monoclinic transformation temperature M_S increases with increase in zirconia grain size in both zirconia toughened aluminas and polycrystalline tetragonal zirconias. The rate of increase is influenced by the Young's modulus and thermal expansion mismatch. Data were obtained via low-temperature dilatometry.

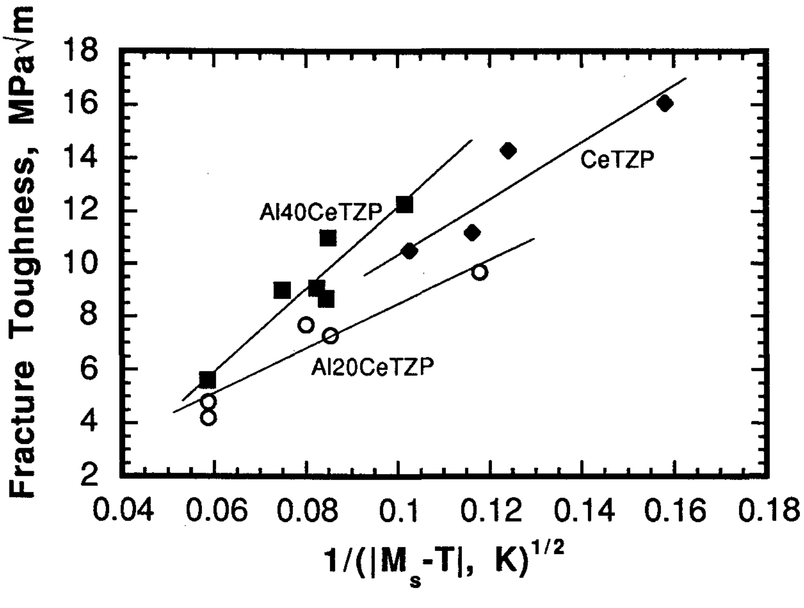


Fig. 4. The transformation toughening contribution to the fracture toughness at 22°C of both the ZTA and TZP ceramics increases as the M_S temperatures are increased by growth of the zirconia grains. The toughness values are plotted here against the square root of the absolute value of the term ($M_S - T$).