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TOUGHENING OF NANO-COMPOSITE CERAMICS

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ABSTRACT

In this paper, the toughening of zirconia ceramics with dispersed silicon carbide nano-particles is studied. Based on both the experimental observations, three effects of nano-particles on the toughness of nano-composite ceramics, namely, nano-particle clustering, crack pinning and transgranular fracture, are identified from both the experimental and analytical studies. And a model considering the above toughening effects is developed to predict the overall toughness of nano-composite ceramics.

KEYWORDS

Toughening mechanism, ceramic, fracture, nano-particle, composite, clustering.

INTRODUCTION

Since nano-composite ceramics were first made in1980’s, the experiments carried out by many researchers, e.g., Izaki et al. [1], Niihara [2], Sawaguchi[3], Zhao et al. [4], and Tian [5], have shown that the ceramic matrix can be significantly toughened by dispersing nanometer sized particles in it to form nano-composite ceramics. The toughening mechanisms of such process have attracted the interest of many researchers. Niihara et al. [2] found that not all nano-particles were distributed within the matrix grains but also along the grain boundaries. Niihara et al. [2] and Zhao et al.[4] concluded that the switch of fracture pattern from intergranular to transgranular, due to the existence of nano-particles along the grain boundaries, is the main toughening mechanism. In comparison with the experimental work, there is a lack of theoretical modelling due to mathematical complication. Pezzotti [6] proposed a “bridging” model and argued that the “bridging” effect of the nano-particle near a crack tip is the main toughening mechanism. The most valuable theoretical work on examination of toughening mechanisms was done by Tan and Yang [7] who highlighted some toughening mechanisms. In this paper, the toughening of zirconia ceramics with dispersed silicon carbide nano-particles is studied. Based on both the experimental observations done by the authors and other researchers and the theoretical modelling proposed by Toya [8], Cotterell and Rice [9], Sumi [10] and Tan and Yang [7], the toughening mechanisms of nano-composite ceramics are analyzed. And a model, in which three toughening effects, i.e., nano-particle clustering, crack pinning, and transgranular fracture induced by nano-particles, is developed to predict the overall toughness of nano-composite ceramics.

EXPERIMENTAL OBSERVATION

The nano-composite ceramics with zirconia (Z_rO_2) matrix and silicon carbide nano-particles were fabricated by the coagulation casting approach [1]. The Young's modulus and Poission's ratio of the zirconia matrix are E_m=400GPa and $\nu_m = 0.25$, respectively, and the corresponding values of the nano-SiC particles are E_p=440GPa and $\nu_p = 0.17$. The zirconia ceramic, which consists of 0% nano-particle, and the nano-composite ceramics with 2%, 5%, 10%, 20% volume fraction of nano-particles were produced at the sintering temperatures of 1600^{0}C, 1650^{0}C, 1700^{0}C, 1750 ^{0}C, and 1800^{0}C, respectively. The average size of the SiC nano-particle and the zirconia matrix grain were 60 nanometers (nm) and 3 μm, respectively. The strength of the nano-composites with different volume fractions of nano-particles was measured using three-point-bending specimens with length 36mm, height 4mm and thickness 4.0mm. Figure 1 shows the average bending strength of the nano-composite with respect to the volume fraction of the dispersed nano-particles. Note that each experimental point represents the average measured value of nine specimens. The fracture toughness was obtained from the indentation test, which has been accepted as a standard test for toughness measurement of brittle materials [12]. Figure 2 demonstrates the toughness of nano-composites with respect to the volume fraction of the dispersed nano-particles. It can be seen from the experimental data in Fig.1 and 2 that both the strength and toughness increase with increasing volume fraction of nano-particles. However, the strength reaches its highest value at V_f=10%. The fracture surfaces of the specimens used in three-point bending tests were examined using a scanning electronic microscope. It can be found from SEM observation that the ZrO_2 matrix grains are refined by the addition of nano-particles. The transgranular cracking increases with increasing volume fraction of nano-particles, and the fracture surface at the scale of each grain has many irregular steps, i.e., the fracture surface becomes more blurry. Figure 3 shows the TEM images of ZrO_2/nano-SiC composite ceramics. Figure 3(a) clearly illustrates the clustering of nano-particles within the grains; Fig. 3(b) clearly shows the inter/intra distributions of nano-particles; and Fig. 3(c) reveals crack pinning due to nano-particles.

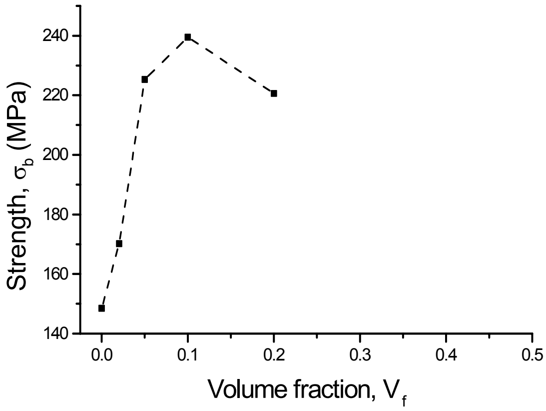


Fig.1: Strength of the Z_rO_2/nano-SiC ceramics

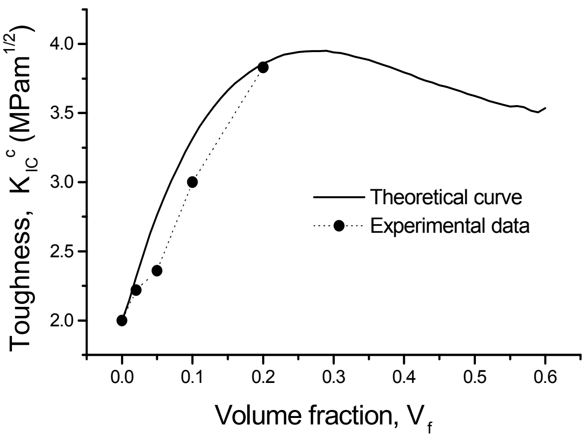
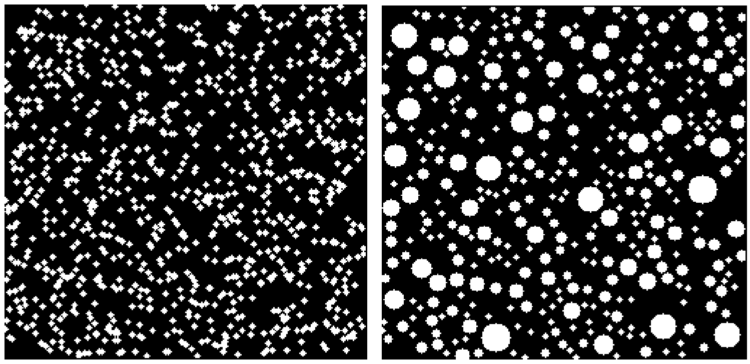


Fig. 2 Toughness of the Z_rO_2/nano-SiC ceramics

(a) (b) (c)

Fig. 3: TEM images of ZrO_2/nano-SiC composie ceramics: (a) clustering of nano-particles. within the grains; (b) inter/intra distributions of nano-particles; (c) crack pinning of nano-particles.

ANALYSIS



(a) (b)

Fig.4: Nano-particle clustering operation for V_f =30%.

Effects of nano-particle clustering

Assume that the nano-particles with an average size, d_p, are randomly distributed. The random distribution can be produced in the following manner. At the initial state, the two-dimensional coordinates (x_i, y_i) for each nano-particle with radius, $r_i = r_p$, is introduced into the representative element by a randomizer, as shown in the left-hand column of Fig. 4. The plane size of the representative element is $1000r_p \times 1000r_p$ in which the total number of nano-particles, N^{total}, is about 320000 when the volume fraction, V_f, reaches 100%. After randomly distributing the nano-particles, an approach is adopted to statistically record the clustering. Two arbitrary nano-particles, i, j , with radii r_i and r_j, respectively, are deemed to be in contact if the coordinates of the two particles satisfy $(x_i - x_j)^2 + (y_i - y_j)^2 < (r_i + r_j)^2$. When two particles are in contact with each other, a new particle, k, is formed replacing particles i and j. Once two particles are combined, the radius and coordinates of the new particle, k, can be determined by

$$x_k = x_i \frac{r_i^2}{r_i^2 + r_j^2} + x_j \frac{r_j^2}{r_i^2 + r_j^2}, \quad y_k = y_i \frac{r_i^2}{r_i^2 + r_j^2} + y_j \frac{r_j^2}{r_i^2 + r_j^2}, \quad r_k = \sqrt{r_i^2 + r_j^2} \tag{1}$$

This clustering process continues till no particles are in contact with each other. Upon completion of this process, a new random distribution is formed, as shown in the right-hand column of Fig. 4. Obviously, in the new clustering distribution, the total number of nano-particles becomes lesser while the average size of the particles becomes larger. For an original random distribution of m nano-particles with a given volume fraction V_f, the average radius, $\bar{r}_{clustering}$, of the clustered particles in the new distribution can be calculated by $\bar{r}_{clustering}(V_f) = \sqrt{\dfrac{V_f A_0}{\pi N^{agg}}}$, where A_0 is the area of the representative element and N^{agg} is the the number of the clustered nano-particles. Note that each clustered nano-particle may consist of n nano-particles ($n = 1,2,3,........$). For each and every step of the statistical clustering process, two parameters, which are important to the toughening analysis to be carried out later, are to be recorded. One is the volume fraction, V_f^n, of the clustered nano-particles (with radius $\bar{r}_{clustering}$), each of which consists of n nano-particles with radius r_p. The volume fraction is given by $V_f^n = nN^n / N^{total}$, where N^n is the number of the clustered nano-particles, each of which consists of n original nano-particles. It is obvious that $V_f = \sum_n V_f^n$. The other is the probability of crack pinning, p_n, which defines the chance that a crack is impeded by a nano-particle and, thus, cannot pass through the nano-particle. The probability is defined as $p_n = \dfrac{1}{n^2}$. If $n = 1$, there is no clustering, i.e. $p_n = 1$, which means that the crack cannot pass through the nano-particle. The larger the value n, the smaller is the probability p_n. In other words, the larger the size of the clustered particle, the more defects it contains and, thus, the easier it is for the crack to pass through the clustered particle. Therefore, p_n reflects the effect of nano-particle clustering.

Effects of crack pinning of nano-particles

When a main crack is pinned by a nano-particle, the nano-particle may be pulled out from the matrix since the crack cannot penetrate directly through the nano-particle. In the initial pull out stage, an interfacial arc-crack appears at $\theta = \pm\pi/4$ and $r = d_p/\sqrt{2}$. For an arc-crack subtending an angle 2α, Toya [8] has established the following formula to calculate the energy release rate J:

$$\frac{J}{J_0} = \frac{k^2}{8}\left(1+4\omega^2\right)\left[1+\frac{(1+\kappa_2)}{(1+\kappa_1)\Gamma}\right]N\exp[2\omega(\pi-\alpha)]\sin\alpha = F(\alpha) \tag{2}$$

where $\kappa_1 = 3-4\nu_1$, $\kappa_2 = 3-4\nu_2$, $\Gamma = \dfrac{\mu_2}{\mu_1}$, $\omega = -\dfrac{\ln(\nu)}{2\pi}$, and the parameters k, N and ν are given in Toya's paper [8], μ_1, ν_1 are the shear modulus and Poisson's ratio of the matrix, respectively, and μ_2, ν_2 are the corresponding values of the nano-particle. The energy release rate for a crack of length d_p in the matrix is given by $J_0 = \frac{(1-\nu_1)\sigma_y^2 \pi d_p}{4\mu_1}$. When J reaches the critical value J^c at the interface between the matrix and the nano-particle, the main crack will connect to the arc-crack along the interface, leading to the "pull-out" of the nano-particle from the matrix. In this case $J = J^c$, the "pull-out" stress and stress-intensity-factor can be obtained as follows:

$$\sigma_y = \sqrt{\frac{4J^c \mu_1}{(1-\nu_1)\pi d_p F(\alpha)}}, \quad K_{nano} = \frac{1}{0.593278}\sqrt{\frac{4J^c \mu_1}{(1-\nu_1)\pi F(\alpha)}} \tag{3}$$

It is obvious that crack pinning gives rise to toughening because a higher stress intensity factor is required for a crack to pass through a nano-particle leading to "pull-out" of the nano-particle. Indeed, the numerical calculation indicates that K_{nano} is much larger than that of the matrix ceramics.

Transgranular fracture induced by nano-particles

The experimental results showed that the nano-particles along the grain boundaries steer the crack to propagate into the matrix grains [3-4,7]. Note that the procedure adopted in the analysis of transgranular fracture is similar to that employed by Cotterell and Rice [9], Sumi [10] and Tan and Yang [7] for the analysis and discussion of kinked and transgranular fractures. By considering the mechanism of transgranular fracture, the overall toughness of the nano-composite ceramic can be expressed as [7]

$$\bar{J} = (f^{ins} + f^{\text{int}} V_f) J_1^{ins} + f^{\text{int}}(1 - V_f) J_1^{\text{int}} \tag{4}$$

where J^{int}, J^{ins} denote the fracture energy of the grain boundary and that of the lattice with no existence of nano-particles, respectively. f^{int} , $f^{ins} = 1 - f^{\text{int}}$ are fractions of the intergranular and the transgranular fracture, respectively. V_f stands for the area percentage, . For zirconia ceramics, the values are $J_1^{\text{int}} = 18.28$ Jm^{-2} and $J_1^{ins} = 48.07$ Jm^{-2} from formula given in [.

Toughening of nano-composite ceramics

The three effects of nano-particles on the toughness of nano-composite ceramics discussed above can be combined to obtain a general formula for calculating the overall toughness of such ceramics. Thus, the critical stress intensity factors for intergranular fracture, K_c^{int}, and transgranular fracture, K_c^{ins}, are given by

$$K_c^{\text{int}} = (1 - V_f) K_{(1)}^{\text{int}} + \sum_n \left(V_f^n p_n K_{nano} + (1 - p_n) V_f^n K_{(2)}\right), K_c^{ins} = (1 - V_f) K_{(1)}^{ins} + \sum_n \left(V_f^n p_n K_{nano} + (1 - p_n) V_f^n K_{(2)}\right) \tag{5}$$

where subcript 1 and 2 denote the matrix and nano-particle, respectively. Thus, $K_{(1)}$ and $K_{(2)}$ are the critical stress intensity factors of the matrix ceramic and nano-particle materials, respectively. Note that

$$K_{(1)}^{\text{int}} = \sqrt{E_1 J_1^{\text{int}} / \left(1-\nu_1^2\right)}, \quad K_{(1)}^{ins} = \sqrt{E_1 J_1^{ins} / \left(1-\nu_1^2\right)} \tag{6}$$

The overall toughness of nano-composite ceramics can be calculated by combining equations (5) and (6) as follows:

$$K^c = \left[\left(1 - f^{\text{int}} + f^{\text{int}} V_f\right)\left(K_c^{ins}\right)^2 + f^{\text{int}}\left(1 - V_f\right)\left(K_c^{\text{int}}\right)^2\right]^{1/2} \tag{7}$$

Figure 2 shows that the solid curve, which was plotted using equation (7), for the ZrO_2/nano-SiC composite ceramics agrees with the corresponding experimental data represented by the solid circles. The theoretical prediction indicates that the toughness reaches its maximum value when the volume fraction of the nano-particles equals 25%. Note that in the calculations, the size of the nano-particle was assumed to be 60 nm in average diameter, and that of the matrix grain was 3 μm in average diameter.

CONCLUSIONS

The toughness of nano-composite ceramics may be influenced by many factors, e.g., the size, volume fraction and distribution pattern of the nano-particles, etc.. Three effects of nano-particles on the mentioned toughness, namely, nano-particle clustering, crack pinning and transgranular fracture, are identified from both the experimental and analytical studies. The propagation of a crack may be pinned by the nano-particles near the crack tip. Crack pinning leads to pull-out of a nano-particle. Transgranular fracture increases with the increase of the volume fraction of nano-particles. Since the fracture resistance of the grain boundary is lower than that of the grain lattice, the higher the probability of transgranular fracture induced by nano-particles, the tougher is the nano-composite. Nano-particle clustering, which increases with increasing volume fraction of nano-particles, leads to the reduction of both the strength and toughness of the nano-composite ceramics. The larger the size of the clustered particle, the more defects it contains and, thus, the easier it is for the crack to pass through the clustered particle.

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