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Microstructure and mechanical properties of yttria-stabilized tetragonal zirconia polycrystals containing dispersed TiC particles

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The microstructure and mechanical properties of hot-pressed yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) ceramics containing up to 30 vol % TiC particles were studied. Adding TiC particles to Y-TZP improved the bending strength and fracture toughness. With 20 vol % TiC particles the maximum bending strength and fracture toughness reached 1073 ± 30.4 MPa and 14.56 ± 0.25 MPa $m^{1/2}$, respectively. The residual tensile stress induced by the thermal expansion difference between ZrO_2 and TiC must have inhibited the tetragonal–monoclinic transformation. The stress-induced phase transformation was therefore not the dominant toughening mechanism. High-densities of dislocations within TiC particles and microcracking were detected by TEM. The improved toughness of the materials is considered to be the result of crack deflection, crack bowing of TiC particles and microcracking toughening of ZrO_2.

1. Introduction

Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) can be tailored in a variety of strength/toughness values, which essentially depend on the grain sizes and Y_2O_3 content [1, 2]. Unfortunately, these excellent mechanical properties are superior to most other ceramics only at ambient temperatures. With increasing temperature, the properties of all TZP materials generally degrade, due to the reduction of the thermodynamic driving force and the fact that the stress-induced transformation becomes less effective. One of the various strategies to strengthen and toughen zirconia ceramics at higher temperature is the incorporation of particles, platelets or whiskers with high moduli within the microstructure [3]. Carbide particulate additions are one possibility. In the choice of carbides, TiC was selected for the investigation because of its high hardness, low density, and excellent oxidation resistance. It is also expected that such second-phase inclusions may enhance fracture toughness at room temperature by crack deflection and a microcracking effect [4]. This paper reports the results of an investigation on the microstructure and properties of TiC_p/Y-TZP composites, fabricated from coprecipitated powders.

2. Experimental procedure

The chemical composition (weight per cent) and average particle size of the powders used to produce the composites are presented in Table I. The composition was analysed on the basis of calibration curves by X-ray fluorescence, using standard samples with different compositions. The starting ZrO_2 powders stabilized with 3 mol % Y_2O_3 and TiC powders were mixed in an attritor mill using ZrO_2 mill balls in a medium of isopropanol. After cold isostatic pressing, the green compacts of TiC_p/Y-TZP composites containing 10, 20, and 30 vol % TiC particles, were hot-pressed at 1700 °C, 30 MPa under argon for 40 min. All the pressed samples were ground and polished before testing. The density was determined by Archimedes' method; Vickers hardness was measured by indentation with a load of 98 N. The bending strength was measured by a three-point bending test (span 30 mm, loading speed 100 N s^{-1}) with a sample geometry of $36 \times 6 \times 3$ mm^3. Fracture toughness was measured by four-point bending of specimens with a sharp and straight precrack, which was introduced by the bridge method [5]. Stress-induced tetragonal to monoclinic (t–m) phase transformation on the fracture surface was evaluated by using the method developed by Garvie and Nicholson [6].

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TABLE I Chemical composition and average particle size of powders used to produce the composites

Materials	Composition (wt %)											Size (μm)
	ZrO_2	SiO_2	Fe_2O_3	TiO_2	Na_2O	Cl	H_2O	Ti	Fe	C	N	
Y_2O_3–ZrO_2	Bal.	0.02	0.03	0.03	0.05	0.06	0.5					0.4
TiC								Bal.	0.11	19.78	0.18	1.84

Phase identification was accomplished by optical microscopy, scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDAX). The TEM foils were taken from the fractured bending specimens at a location in the inner span, where the bending moment is constant.

3. Results and discussion

3.1. Microstructural characteristics

It is well-known that thermal expansion mismatch between particle and matrix causes residual stress within and around the particles when the composite cools down from its fabrication temperature. For the case of a single, spherical particle of radius R in an infinite isotropic matrix, a uniform stress, $-\sigma$, arises within the particle, and radial and tangential stresses of $-\sigma R^3/r^3$ and $\sigma R^3/2r^3$, respectively, arise around the surrounding matrix, where r is the distance from the centre of the particle to a point in the matrix [7]. These equations represent a satisfactory approximation for the residual thermal stress set up during cooling of the composite containing low concentrations of particles. The stress, σ, is given by

$$\sigma = \frac{(\alpha_m - \alpha_p)\Delta T}{\left(\frac{1+\nu_m}{2E_m} + \frac{1-2\nu_p}{E_p}\right)} \tag{1}$$

where the subscripts m and p represent matrix and second phase particle, respectively, α and E are the thermal expansion coefficient and Young's moduli, ν is Poission's ratio, ΔT is the temperature difference between processing and room temperature. The parameters α, ν and E of Y-TZP and TiC are given in Table II [8]. Thus, in the present composite systems where $\alpha_m > \alpha_p$, the particle is subjected to a compressive stress and the matrix to radial compressive and tangential tensile stresses. It is then expected that the tangential tensile stresses can induce radial microcracks in the matrix around each particle. However, it has been observed that such microcracks only form adjacent to the larger particles and not near to the smaller ones. This problem was considered by Lange [9] on the basis of an energy balance concept. He derived a relation which describes a condition or crack formation during cooling as follows:

$$\sigma^2 D \geqslant \text{constant} \tag{2}$$

where D is the particle size. Equation 2 indicates that for a given particulate composite system, there will be a critical particle size below which microcracks are not formed.

TABLE II Properties of Y-TZP and TiC

Materials	α (10^{-6} K)	E (GPa)	ν
Y-TZP	10	200	0.23
TiC	7.4	460	0.19

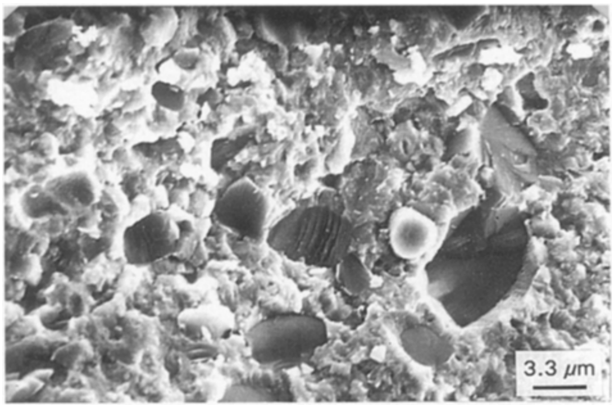

Figure 1 SEM image showing the microstructure of 20 vol % TiC/Y-TZP composite produced by hot-pressing.

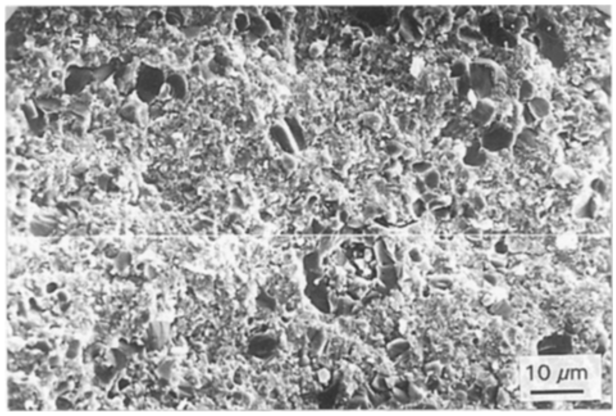

Figure 2 SEM image showing clustering of TiC particles with 30 vol % TiC/Y-TZP composite.

Fig. 1 shows the typical microstructure of ZrO_2–TiC particulate composites which shows TiC grains with an average size of 2.05 μm uniformly dispersed in ZrO_2. No significant influence of TiC additions on the grain growth of the matrix was observed. The average grain size of the matrix is 0.5 μm. In this composite system where α_m–$\alpha_p = 2.6 \times 10^{-6}$ K^{-1}, no microcrack formation during cooling was recognized for the specimens containing lower volume fractions of dispersed particulates. At higher concentrations of particles, microcracks were observed only at a few locations. These exceptional cracks at higher concentrations are probably due to local clustering of

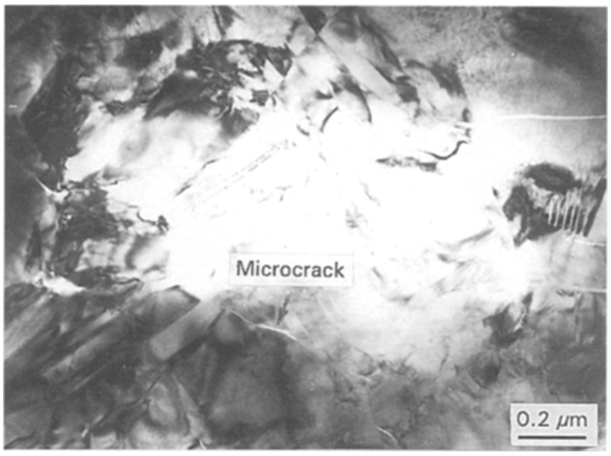

Figure 3 TEM image showing microcracking associated with the t–m transformation of zirconia after the bending test.

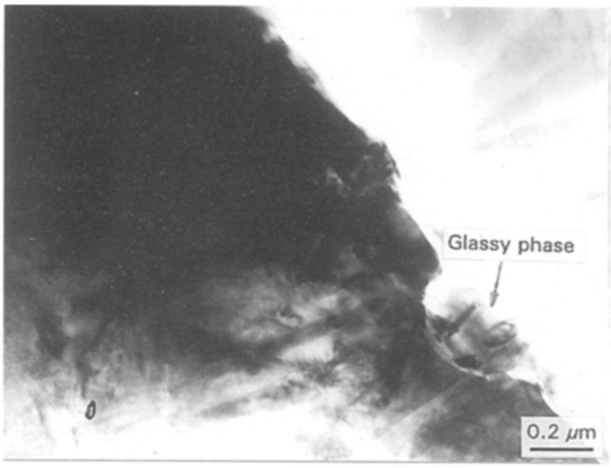

Figure 4 Grain-boundary phase is TiC/Y-TZP composite.

particles (Fig. 2), which may lead to the overlapping of strain-energy fields.

Additions of less than 10 vol % TiC particles caused the sintered densities to decrease dramatically because of the formation of numerous pores and large voids. All the other samples have reached a relative density of 99.5%. The Y-TZP matrix was almost completely in the tetragonal phase after the densification process. The microstructure of the composites was again studied after bending. The TEM image revealed the t–m transformation of zirconia, associated with microcracking, as illustrated in Fig. 3. There are two reasons for the occurrence of microcracking. The first is the stress-induced t–m transformation with a dilatational volume change. The second are the residual stresses (radial compressive stress and tangential "tensile" or "shear" stress) due to thermal mismatch between zirconia and TiC. If the densification temperature is 1700 °C, tensile stresses in the matrix as high as 200 MPa will be expected for $v = 0.2$, where v represents volume fraction of TiC. It seems that the condition for microcrack formation during cooling is not met for TiC_p/Y-TZP composites. It is well known that tensile stress can benefit the nucleation of monoclinic zirconia, and hence, the t–m transformation [10]. Internal stresses react additively to the external load in opening and propagating the crack.

At the phase boundaries between zirconia and TiC, an amorphous phase was detected by TEM, as shown in Fig. 4. The possible sources of this glassy phase are the sintering reaction between zirconia and TiC, and the resultant phase changes such as oxygen-deficient zirconia [11].

The influence of glassy phase can be very different. It can improve the densification process, but also enhance grain growth [12]. Claussen *et al.* [13] reported that the high-temperature strength can be improved by the softening of glassy grain-boundary layers by activating some load transfer. The creep resistance, however, will be reduced. Furthermore, the formation of liquid phases during sintering may lead to beneficial agglomerate formation, i.e. the flaw size will be increased [14].

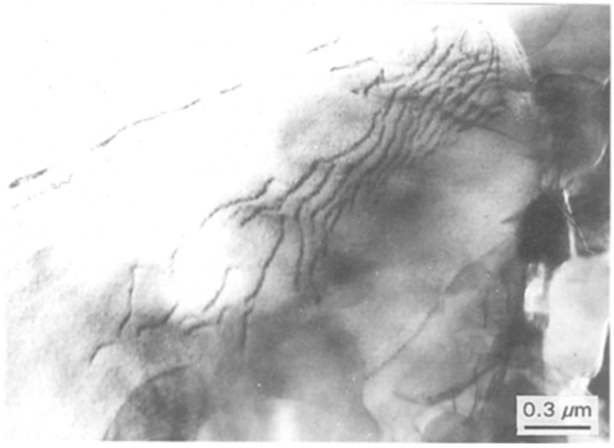

Figure 5 Dislocations in the TiC particles.

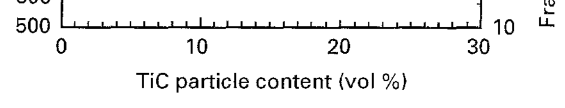

Figure 6 The effect of TiC addition on (◇) fracture toughness and (○) strength of composites.

Many dislocations in the TiC particles were also discovered by TEM (Fig. 5). This indicated that the mechanism of the momentary pinning of the moving crack front by these particles is the operative toughening mechanism, i.e. crack bowing.

3.2. Mechanical properties

As shown in Fig. 6, the strength in TiC_p/Y-TZP ceramics shows a maximum at 20 vol % TiC. Above 20 vol %, the strength decreased because of poor

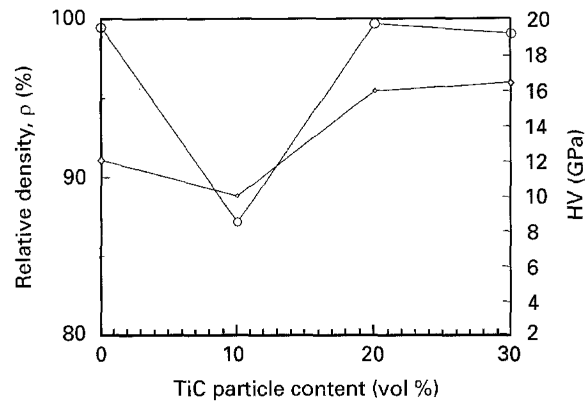

Figure 7 (○) Relative density and (◇) Vickers hardness, HV, of the composites.

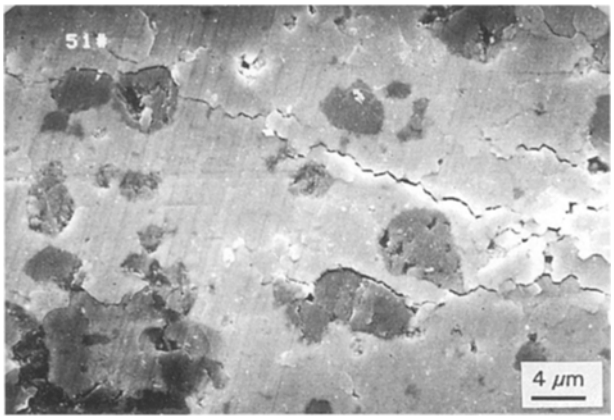

Figure 8 SEM image showing crack deflection in the 20 vol % TiC/Y-TZP composite.

sinterability of TiC. The fracture toughness increases with increasing TiC content up to 20 vol % TiC and then decreases. Additions of less than 10 vol % TiC caused the sintered densities and strength to decrease dramatically. The density and strength degradation evident in Fig. 6 can be attributed to reactant gas liberated between zirconia and TiC, as well as liberation of nitrogen gas in TiN_{1-x}–Ni sintered alloys [15]. The fracture toughness could not be measured below 10 vol % TiC because of high porosity.

As a representative example, we show the microstructure of 20 vol % TiC_p/Y-TZP, giving a maximum strength as shown in Fig. 1, where a network of TiC grains with an average size of 2.05 μm is uniformly dispersed in zirconia matrices. Also, spontaneous microcracking, which might be caused by thermal residual stresses, was not detected for the specimens containing 20 vol % TiC. Judging from these results, the reason for an increase in strength at 20 vol % TiC may be based on this continuous skeleton of TiC.

Vickers hardness and relative densities of sintered TiC_p/Y-TZP composites are shown in Fig. 7 to follow the same trend. Because of the sensitivity of the strength of ceramic materials to flaws, this improvement of density can lead to a large increase in strength, and hence, increase of Vickers hardness.

To investigate possible mechanisms responsible for toughening, the ratio of $m\text{-}ZrO_2$ to $t\text{-}ZrO_2$ phase on the fracture surface was determined by X-ray diffraction phase analysis. The results indicated that the $m\text{-}ZrO_2$ content decreased with increasing TiC content. Above 20 vol % TiC addition, t–m transformation was not the dominant toughening mechanism. Because the residual tensile stress in the composites up to 30 vol % TiC content is very large, the stress must lead to the t–m martensitic transformation during the cooling process. The principle of residual stress toughening of ceramics is the introduction of compressive residual stress by thermal expansion mismatch [10]. This requires that the matrix exhibits a lower thermal expansion than the incorporated particles. In the TiC-toughened Y-TZP composites, just the opposite is realized. In spite of the incorrect thermal mismatch and the reduced stress-induced phase transformation, the fracture toughness of Y-TZP is significantly increased by the incorporation of TiC particles. The toughening mechanism appears to be crack deflection (as shown in Fig. 8) and possibly some microcracking, and crack bowing.

As seen from Fig. 8, elastic modulus and thermal expansion mismatch between constituent phases of composites may cause the crack to deflect around second-phase particles. This contributes to toughening of ceramics. The interaction of the primary crack front with pre-existing and/or transformation-induced microcracks may contribute to toughening of brittle materials [6, 10]. In TiC_p/Y-TZP composite containing 20 vol % TiC content, the transformation-induced microcracking is very effective in toughening the brittle materials. Experiments also suggested that the fracture toughness of composites might be considerably increased when particles slightly larger than the critical size predicted from Equation 2 are dispersed. In this case, K_{1c} increases with a certain volume fraction, presumably because the microcrack density within the process zone reaches a critical level. On the other hand, in the case of the dispersion of particles smaller than the critical size, stress-induced microcracking may occur, but microcrack toughening for this case is not effective unless the particle size is close to the critical size [10].

4. Conclusions

1. Adding TiC_p to Y-TZP improved not only strength and hardness but also fracture toughness. When TiC particles are distributed uniformly in the Y-TZP matrix, the composites have excellent mechanical properties. The strength and fracture toughness of the composite containing 20 vol % TiC particles are 1073 ± 30.4 MPa and 14.56 ± 0.25 MPa $m^{1/2}$, respectively.

2. Even with incorrect thermal mismatch and a reduced stress-induced phase transformation, the fracture toughness Y-TZP was significantly increased by TiC particles. The main toughening mechanism appears to be crack deflection, possibly some microcracking and crack bowing. Stress-induced phase transformation played only a secondary role.

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