

Influence of tungsten carbide particles on resistance of alumina matrix ceramics to thermal shock

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Abstract

The mechanical properties and thermal shock behavior of the hot pressed alumina matrix ceramics, with added 6 vol.% tungsten carbide particles, was investigated. The thermal shock resistance of the materials was evaluated by water quenching and subsequent three-point bend testing of flexural strength diminution. The hot-pressed composite exhibited 70°C higher temperature differential of thermal shock resistance than the monolith, as well as increased flexural strength and fracture toughness. The calculation of thermal shock resistance parameters for the composite and the monolith gives a possible explanation for the differences in thermal shock behaviour. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

It has been known that the incorporation of a second phase particulate into a ceramic matrix can bring about improvement on ceramics mechanical properties for many years. The most promising composites of this type are those with a higher degree of ductile particles bridging across parting crack faces in the wake of a propagating crack. The addition of a secondary phase into a ceramic matrix has been indicated to improve the resistance to crack propagation in various ways.^{1–6} Improvement on fracture toughness is also attributed to the mechanisms of crack blunting, shielding and crack deflection accompanied by particle pulling-out etc.^{2,7–9} Extensive work pertaining to the mechanical properties of a second-phase particle toughened ceramic matrix composite, has been carried out, but rare studies are known with respect to thermal shock resistance, which is very important if the material is used in thermal fluctuating environments.

The classic theory on the thermal shock resistance of brittle ceramics was established by Hasselman.¹⁰ The work showed opposing property requirements for

materials, depending on whether the material was required to be resistant to crack initiation or resistant to strength degradation after a severe thermal shock. The conditions for stable and unstable crack growths were predicted based on the idea that the driving force for crack propagation was provided by the stored elastic strain energy. In the theory, some thermal shock resistance parameters (*R* parameters) were defined to relate thermophysical and thermomechanical properties of a brittle material to its thermal fracture resistance.¹¹

As we know, alumina ceramics, one of the most successful engineering ceramics, have great potential to be used in many special applications where low density, high stiffness, high hardness, chemical inertness and good high-temperature properties are required.^{12,13} Tungsten carbide, a common hard alloy powder, is extensively utilized in machine tools and protective coatings because of its high hardness, desirable chemical stability and fine abrasion resistance.¹⁴ The present work was undertaken to assess the thermal shock behavior of alumina matrix ceramics with near-theoretical density incorporated with tungsten carbide particles. Comparative experiments were carried out with reference to monolithic alumina ceramics. Thermal shock susceptibility was quantitatively assessed as a function of quenching temperature from strength degradation in three-point bend tests. It was shown that the tungsten

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carbide addition and the scale of microstructure played significant roles in modifying the strength diminution response observed in alumina ceramics.

2. Experimental

The alumina-tungsten carbide composite and monolithic alumina ceramics were all produced by hot-pressing during the current study. The alumina powder (99.92% purity, 0.4 μm , Shanghai Wusong Chemical Co., China) and common tungsten carbide particles (99.50% purity, 5.0 μm , Shanghai Plant of Metallurgy, China) were ball-milled with ethanol for 12 h using high purity alumina balls as the grinding media in a polyethylene pot, to form a consistent slurry. The milled slurry was then sieved through a 45 μm sieve and oven-dried for 48 h at 90°C. After drying, the agglomerated powder was crushed and screened through a 150 μm sieve for subsequent sintering. The composite powder mixture and the monolithic alumina powder were packed in a graphite die that was coated with BN and hot pressing experiments were conducted at 1450 and 1550°C for 1 h under 12 MPa of applied pressure in a flowing nitrogen-gas atmosphere, respectively.

The hot-pressed bodies were cut, ground with a diamond wheel and polished using diamond pastes. The final diamond lap had an abrasive particle of size 0.5 μm before fracture strength testing and the specimen edges were slightly beveled on a 1200-grit emery paper to remove notches introduced in the course of machining. Bars for testing were heated to the desired temperatures and held for 1 h in a drop-bottom furnace and then quenched into a container of water at room temperature. The thermal quenching was performed at temperatures from 20 to 520°C, which corresponded to thermal shock temperature differences (ΔT) of 0–500°C relative to room temperature, taken as 20°C. At least five samples were tested for each temperature difference. The as-shocked bars were dried at 110°C for 2 h and cooled down in air before residual flexural strength was measured.

The flexural strength of the two specimens was determined by using a conventional three point loading fixture on Instron 1195. The dimensions of all tested specimens were 3×4×36 mm, with a loading span of 30 mm and cross-head speed of 0.5 mm/min. The fracture toughness of the specimens was measured by indentation fracture method with a Vickers' hardness tester.

Characterizations of the hot pressed composite and monolith included X-ray diffraction (XRD, Siemens D-5000, Siemens, Karlsruhe, Germany; $\text{CuK}\alpha$ radiation with a Ni filter) for phase identification, scanning electron microscopy (EPMA-8705QH₂, Shimadzu, Japan) for microstructural observations. The XRD pattern was obtained from the as-sintered surface of the composite.

SEM micrographs were taken from ground, polished, thermally etched and Au-coated surfaces. The densities of the sintered samples were measured by using Archimedes' method in deionized water, and the theoretical density was calculated by applying the law of mixture to the volume fractions of the constituents.

3. Results and discussion

3.1. Microstructure features and mechanical properties of the materials

3.1.1. Microstructure features

Fig. 1 is the XRD pattern of the hot pressed composite. There are no third characteristic peaks in addition to the peaks of $\alpha\text{-Al}_2\text{O}_3$ and WC. This result shows that no new phase has been formed in the course of the hot-pressing sintering between $\alpha\text{-Al}_2\text{O}_3$ and WC. Table 1 summarizes the microstructural features of the two kinds of materials in terms of matrix grain size, tungsten carbide particle size and morphology. Fig. 2 shows a typical microstructure of the hot pressed composite. The microstructure of the $\text{Al}_2\text{O}_3\text{-WC}$ composite consists of an apparently random, but rather homogeneous distribution of irregularly shaped tungsten carbide particles within a dense, fine grained alumina matrix. As to the average grain size, the monolithic alumina grain size is larger than the composite. This phenomenon can be

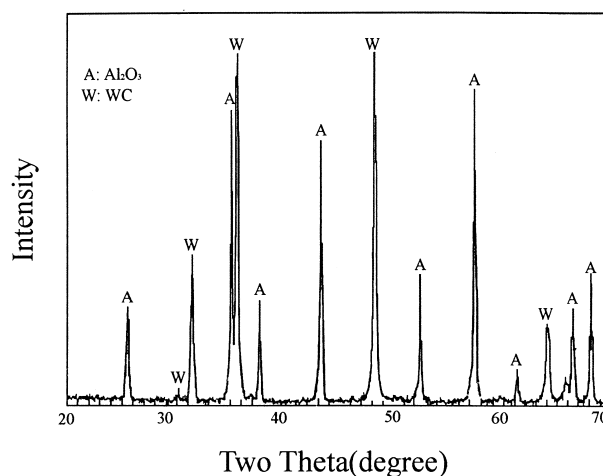


Fig. 1. XRD pattern of as-sintered alumina-tungsten carbide composite.

Table 1

Summary of the density and microstructural features of the hot pressed monolithic alumina and alumina-tungsten carbide composite

	Density (% theoretical density)	Matrix grain size (μm)	WC particle size (μm)	WC particle shape
Monolith	99.8	2.79	/	/
Composite	99.6	1.45	7.70±2.40	Irregular

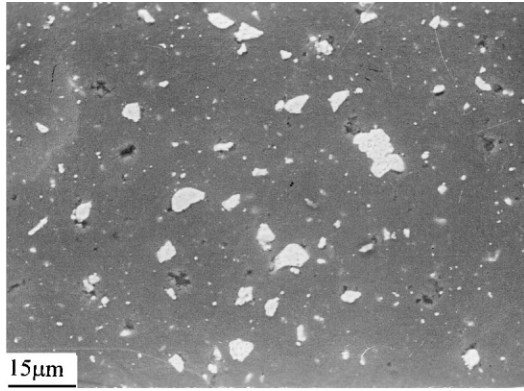


Fig. 2. Photomicrograph of hot pressed alumina–tungsten carbide microstructure (the light areas stand for the WC particles and the grey areas for the alumina matrix).

attributed to the fact that the existence of the second phase in composite inhibits the grain growth of the alumina base.

3.1.2. Flexural strength

The flexural strengths of the test bars were measured by a conventional three point fixture on Instron 1195 and the calculated values of flexural strength can be obtained from the following equation:

$$\sigma = 1.5PL/DH^2 \quad (1)$$

where σ is the flexural strength, P the load measured by the Instron, L the loading span, D the width of the specimens, and H the height of the specimen. In the present investigation, the strengths for the monolithic alumina ceramics and alumina-tungsten carbide composite were found to be 520 ± 25 MPa and 580 ± 29 MPa, respectively. The higher strength of the alumina-tungsten carbide composite can be attributed to the decreased matrix grain size. In terms of the linear intercept technique,¹⁵ the matrix grain sizes for the monolith and composite were 2.79 and 1.45 μm , respectively. It is also believed that the tungsten carbide, as a second phase, inhibited the growth of the alumina matrix and is well bonded to the matrix so as not to act as strength reducing flaws.

3.1.3. Fracture toughness

The fracture toughness of brittle ceramic materials is one of the most sensitive factors to influence the resistance of the materials to thermal shock. For as-shocked heterogeneous alumina-tungsten carbide composite, dynamic or quasistatic crack propagation is determined by the coefficient of crack stability and the parameter of thermal shock damage resistance (R''') as defined by Hasselman.¹⁰

$$R''' \approx (K_{IC}/\sigma_f)^2 \quad (2)$$

where K_{IC} is the fracture toughness, σ_f the fracture strength. In the current work, the values for the composite and the monolith were obtained to be 5.13 $\text{MPam}^{1/2}$ and 3.52 $\text{MPam}^{1/2}$, respectively. It is well recognized that the presence of the tungsten carbide in the composite can, to some extent, prevent the crack propagation by the mechanisms of crack deflection, divergence, blunting and arresting, etc. These mechanisms were partly related to the mismatch of the coefficients of thermal expansion between WC and Al_2O_3 . Therefore the presence of tungsten carbide particles in the composite has led to a fracture toughness increase of 45.7% as compared to the monolithic alumina.

3.2. Critical temperature differential of thermal shock resistance

In the Hasselman's theory, the critical temperature differential of materials after severe quenching is an important index to evaluate the thermal shock resistance. In this study, specimens of hot pressed composite and monolith were subjected to a range of temperature differences during water quenching. The retained flexural strength was then measured in the same way as in Section 2. Thermal shock testing demonstrated that the strength responses of the alumina and the alumina-tungsten carbide composite agree with the expected behavior derived from Hasselman's model.¹⁰ The strength data provided information for ascertaining the influence of microstructure on damage resistance. The thermal shock behavior of the base alumina was consistent and in agreement with previous studies of similar alumina ceramics.^{16–19} Fig. 3 shows a plot of retained flexural strength versus temperature differential (ΔT) for the two kinds of materials. The curve for the monolithic alumina is similar to the reported one in the

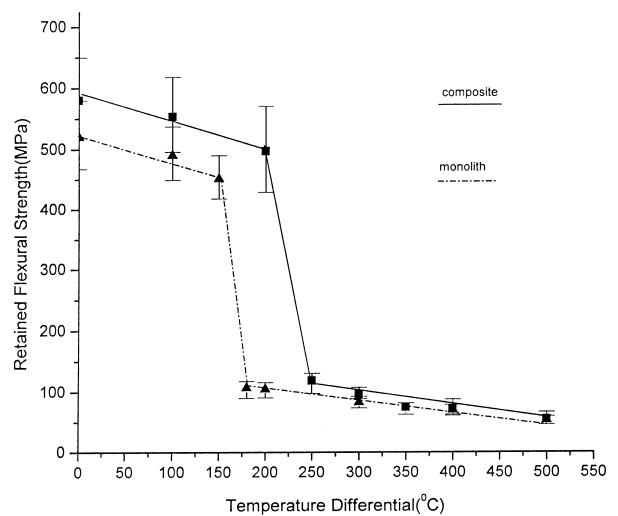


Fig. 3. Plot of retained strength versus temperature differential for hot pressed monolithic alumina and alumina–tungsten carbide composite.

literature,^{16–20} showing a critical temperature differential (ΔT_c) of 175–200°C and characteristic abrupt drop of flexural strength at that point, followed by a modest decrease for further increasing ΔT . Fig. 3 apparently shows that the hot pressed alumina-tungsten carbide composite has a greater resistance to thermal shock in terms of the increased ΔT_c (ΔT_c of the composite is 250°C, 70°C higher than that of the monolith). The addition of tungsten carbide prevented crack propagation, weakened driving force of propagation at crack tips and raised the composite fracture energy. Defective propagation of cracks and the pinning of the secondary particles to cracks are the main factors to improve the thermal shock resistance of the composite (Fig. 4).

3.3. Thermal shock resistance parameters

The effect of microstructure on mechanical properties and the observed thermal shock behavior was quite evident. The addition of tungsten carbide to alumina modified the mechanical properties and, hence, thermal shock behavior. In order to assess the response of a brittle ceramic material to thermal shock, thermal shock resistance parameters (R parameters) were introduced by Hasselman,¹⁰ such that:

$$R = \sigma(1 - \nu)/\alpha E \quad (3)$$

$$R''' = K_{IC}^2/\sigma^2(1 - \nu) \quad (4)$$

where σ is the flexural strength, α the thermal expansion coefficient, E the Young's modulus, ν the Poisson ratio, R''' the fracture toughness. The R parameter is related to the critical temperature differential at which the tensile stress imposed on the surface of the material and presents a measure of the resistance to crack initiation, while the R''' parameter indicates the ability of a material to resist damage following a thermal shock treatment of $\Delta T > \Delta T_c$. Table 2 summarizes the relevant

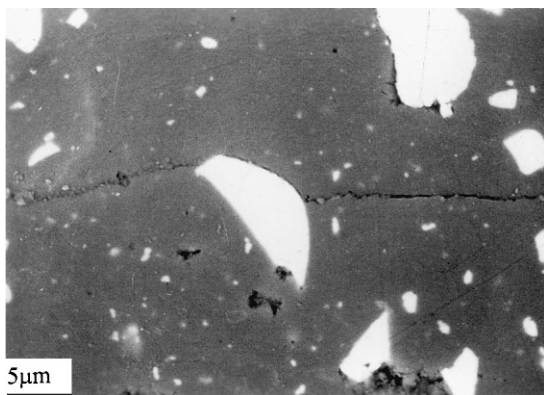


Fig. 4. Photomicrograph showing thermal shock induced crack at $\Delta T = 500^\circ\text{C}$ for hot pressed alumina-tungsten carbide composite.

mechanical and thermal properties of the hot pressed monolithic alumina and alumina-tungsten carbide composite, along with the calculated values of R and R''' . For the simplicity of the calculation, the magnitude of the Poisson ratio for the monolith and composite was supposed to be identical.

From Eq. (3) and Table 2, the addition of tungsten carbide enhanced the flexural strength and reduced thermal expansion coefficient, hence, discernible improvement in the R parameter was found and the critical temperature differential ΔT_c ; meanwhile, the calculated value of R''' parameter is higher than that for the equivalent base alumina. Obviously, the microstructure of the alumina-tungsten carbide composite is also critical to the observed thermal shock response on account of the thermal expansion mismatch and internal residual stresses.¹⁹ Hence, stable crack propagation was possible during water quenching thus leading to a more modest degradation of flexural strength.

4. Conclusions

Monolithic alumina ceramics and alumina-6 vol.% tungsten carbide composite have been fabricated in the method of hot pressing. Some properties and parameters relevant to the thermal shock resistance including flexural strength, fracture toughness, critical temperature differential, R and R''' have been evaluated and discussed. Noticeable differences in the above properties and parameters between the monolith and the composite have been observed and explained in terms of their differences in microstructure.

The critical temperature differential of thermal shock resistance for the alumina-6 vol.% tungsten carbide composite was found to be higher than that for the monolithic alumina ceramics experimentally as much as 70°C. Gained flexural strength and apparently enhanced fracture toughness resulted in the improvement of the thermal shock resistance of the composite. The calculated

Table 2

Summary of relevant mechanical and thermal properties of the hot pressed monolithic alumina and alumina-tungsten carbide composite

	Monolith	Composite
σ_f (MPa)	520 ± 25	580 ± 29
E (GPa)	390 ^b	407 ^a
ν	0.22 ^b	0.22 ^b
K_{IC} (MPam ^{1/2})	3.52 ± 0.25	5.13 ± 0.37
α ($\times 10^{-6}$ K ⁻¹)	7.70 ^b	7.55 ^a
R (°C)	135 ^a	147 ^a
R''' ($\times 10^{-6}$)	59 ^a	100 ^a

^a Theoretically calculated values.

^b Data from Morrell, R., Handbook of Properties of Technical and Engineering Ceramics, HMSO, London, 1985.

R parameters were in good agreement with experimental results of ΔT_c and retained strength at $\Delta T > \Delta T_c$.

Acknowledgements

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