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Thermal shock properties of alumina reinforced with Ti(C,N) whiskers

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Abstract

Alumina composites reinforced with Ti(C,N) whiskers were produced to evaluate the thermal shock properties. The indentation fracture toughness (49 N load) increased from 2.6 MPa $m^{1/2}$ for pure alumina to 5.0 MPa $m^{1/2}$ for the sample with 30 vol.% Ti(C,N) whiskers. The hardness also increased, from 17.6 to 24.2 GPa. A clear R-curve behaviour was observed. An indentation–quench test was used to measure the thermal shock resistance. The best thermal shock resistance was observed at 30 vol.% Ti(C,N) whiskers.

Keywords: Al_2O_3; Composites; Indentation; Thermal shock resistance; Ti(C,N); Whiskers

1. Introduction

Alumina is a brittle material with a poor thermal shock resistance. However, the mechanical properties can be improved substantially by reinforcing it with a phase having good thermal stability, high strength and high elastic modulus. SiC whiskers is the preferred reinforcing phase, especially for cutting tool applications. During the last few years a number of new whisker materials in the form of transition metal carbide and carbonitride phases have been developed, such as TiC and Ti(C,N).[1,2] Such whiskers have high hardness and strength, and they are chemically inert to iron up to high temperatures, making them interesting candidates for reinforcement of ceramic cutting tools.

Many thermal-shock testing techniques use test bars of specified dimensions and geometries. After a heating and quenching procedure the bars are subjected to mechanical testing by e.g. three- or four-point bending-strength tests. These techniques involve some drawbacks: a new test bar is needed for each temperature and, to improve statistics, more than one bar should be tested at each temperature. The technique used in the current work is an indentation–quench method[3] based on indenting small initial cracks on a polished plate. The indented plate is heated in a vertical tube furnace and subsequently quenched in a water bath. The crack length is measured before and after quenching. The indentation–quench method gives data useful for comparing the thermal shock resistance of different ceramic materials. The influence of different experimental parameters on the resolution of this measurement technique has recently been evaluated.[4]

The aim of the present work was to evaluate the thermal shock resistance of alumina composites reinforced with Ti(C,N) whiskers. Another aim was to test the applicability of the indentation–quench test to this type of materials.

2. Experimental

2.1. Starting materials and sample preparation

The Ti(C,N) whiskers were synthesised carbothermally via a vapour–liquid–solid (VLS) growth mechanism according to Ahlén et al.[1,2] The whisker product was analysed chemically for Ti, N, C and O, and the bulk composition was found to be $TiC_{0.21}N_{0.63}O_{0.16}$. The whisker morphology was investigated both in an optical microscope and in a scanning electron microscope

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(SEM, JEOL 820). The whisker yield is estimated to be 80 vol.% and the remaining 20 vol.% is particles of the same compound; the whiskers have a length of 30–40 μm and a diameter in the range 1–3 μm. The matrix material was -Al_2O_3 (AKP-30, Sumitomo Chemical, Inc.).

Composites containing 5–40 vol.% Ti(C,N) whiskers were prepared. In order to suppress alumina grain growth, 0.25 wt.% MgO was added (by Al_2O_3 dry weight).[5] A slurry of Al_2O_3, $Mg(NO_3)_2{\cdot}6H_2O$, and polyacrylic acid dispersant (Dispex A40, Allied Colloids, USA) was mixed by ball milling with Al_2O_3 cylpebs as milling media in deionised water for approximately 18 h. The reinforcing phase was then added to the slurry and the milling was continued for another 5 h. The slurry was then instantly frozen in liquid nitrogen and subsequently freeze-dried.

Before sintering the composite mixtures were heat treated at 600 °C (1 h) in Ar–5% H_2 atmosphere to remove residues of Dispex A40 and to decompose $Mg(NO_3)_2{\cdot}6H_2O$ to MgO before hot pressing.

Green bodies with a diameter of Ø = 12 mm were prepared and sintered in a hot-press furnace (Thermal Technology Inc.) at 1700 °C, 28 MPa, for 90 min.

2.2. Characterisation techniques

The density of all sintered samples was measured by use of Archimedes' principle. Before physical characterisation the specimens were carefully polished by standard diamond polishing techniques down to a diamond particle size of 1 μm.

The microstructure of the composites, in sections both parallel and perpendicular to the pressure directions, was investigated with a scanning electron microscope (SEM, JEOL 820). To obtain the best contrast, the micrographs were recorded in back-scattered electron mode (BSE).

The hardness (H) and fracture toughness (K_{Ic}) at room temperature were evaluated by the Vickers indentation technique at a load of 49 N for all compositions, see Table 1. Five indents were made in a row at the middle (to minimise near-surface effects) of each sample. The fracture toughness was calculated by the indentation method according to Anstis et al.,[6] see Eq. (1).

$$K_{1C} = A\left(\frac{E}{H}\right)^{1/2}\left(\frac{P}{c^{3/2}}\right) \quad (1)$$

A is a constant for Vickers-produced radial cracks (a value of 0.016 has been used[7]), E is Young's modulus, H is the hardness, P is the load and c is the crack length. For the calculations a value for Young's modulus of the whiskers was estimated for a whisker composition of $TiC_{0.25}N_{0.75}$ by assuming a linear relation between the Young's modulus values for TiC (451 GPa) and TiN (612 GPa). Young's modulus for the different composites was estimated by assuming a linear relation between the values for Al_2O_3 (380 GPa) and the reinforcing phase. The R-curve behaviour for two of the whisker composites was determined with loads in the range 35–98 N.

Table 1
Density, hardness, and fracture toughness

Reinforcing phase	Volume fraction (%)	Density (%)	H (GPa)	K_{Ic} (MPa $m^{1/2}$)
–	0	100.0	17.6	2.6
$Ti(C,N)_W$	5	99.5	17.9	2.9
$Ti(C,N)_W$	10	99.6	18.6	3.4
$Ti(C,N)_W$	15	99.7	19.2	4.2
$Ti(C,N)_W$	20	99.9	20.3	4.5
$Ti(C,N)_W$	25	99.6	22.6	4.9
$Ti(C,N)_W$	30	99.7	24.2	5.0
$Ti(C,N)_W$	35	99.6	23.6	5.0
$Ti(C,N)_W$	40	99.8	22.4	4.7

Table 2
Thermal shock parameters: sample thickness, indentation load, and initial crack length

Reinforcing phase	Amount (vol.%)	Sample thickness (mm)	Load (N)	Initial crack length (μm)
–	0	3.90	40	110
$Ti(C,N)_W$	5	4.07	58	128
$Ti(C,N)_W$	10	3.87	58	121
$Ti(C,N)_W$	15	4.15	58	92
$Ti(C,N)_W$	20	4.05	58	101
$Ti(C,N)_W$	25	4.15	58	104
$Ti(C,N)_W$	30	4.17	58	95
$Ti(C,N)_W$	35	4.11	58	97
$Ti(C,N)_W$	40	4.04	58	107

2.3. Thermal shock measurements

Vickers indents were introduced into disc-shaped samples (Ø = 12 mm, h = 4 mm) with parallel surfaces, one of them polished. Each indent generates four cracks, and four indents were introduced on each sample, giving a total of 16 cracks per sample. The crack length is defined as the distance from the centre of the indent to the crack tip. To facilitate comparison between different samples, the initial crack length (l) was held at approximately 100 μm, meaning that the indentation load was varied, see Table 2. The cracks were measured in an optical microscope (Olympus PMG3). Each one was monitored individually, and the total crack length after thermal shock (l_T) was measured and the percentage crack growth (Δc) was calculated, using Eq. (2). If one or two cracks deviated from the

growth of the others, the Student's t-test at 95% confidence was used as criteria to check if they should be included in the calculation of the average crack growth.

$$\Delta c = \frac{l_T - l}{l} \cdot 100 \quad (2)$$

Each sample was hoisted into a vertical tubular furnace and heated to a predetermined temperature (T_F). After 20 min at that temperature the sample was quenched in a water bath at $T_W = 90$ °C, and the cracks were measured to evaluate the growth.

$$\Delta T = T_F - T_W \quad (3)$$

Water close to the boiling point offers quite mild quenching conditions.[4,8] The heating and quenching procedure was repeated with the same sample at stepwise higher and higher T values. It has been shown that the indentation–quench technique allows the same sample to be used for a whole quenching series when the aim is to rank the thermal shock properties of different materials.[4] The samples were heated in air. At the highest temperature used in the experiments, 590 °C, a slight degree of oxidation was observed on the surface of the reinforcing phase, which was not considered severe.

A useful thermal shock parameter is ΔT_X, corresponding to the temperature difference inducing X% growth of the initial cracks. Thus, ΔT_{10} is the thermal shock temperature difference making the cracks grow by 10% of their initial length.

3. Results and discussion

3.1. Microstructure and mechanical properties

The whiskers were homogeneously distributed up to 30–35 vol.% reinforcing phase. However, for the sample containing 40 vol.% whiskers some whisker agglomerates were found, see Fig. 1a–c. This fact may be the reason for the best mechanical properties being found at an addition of 30 vol.% reinforcing phase, see discussion below. During sintering, whiskers arrange themselves perpendicular to the pressure direction. All samples were found to be fully dense.

Both hardness (H) and fracture toughness (K_{Ic}) increase with increasing fraction of reinforcing phase up to 30 vol.%, and then both hardness and fracture toughness decrease again, see Table 1.

The alumina sample without any reinforcing phase has a hardness value of 17.6 GPa and fracture toughness of 2.6 MPa $m^{1/2}$, which may be compared to the sample with 30 vol.% Ti(C,N) whiskers having a hardness of 24.2 GPa and a fracture toughness of 5.0 MPa $m^{1/2}$. This measured fracture toughness, however, is lower than what is generally reported for Al_2O_3 reinforced with 30 vol.% SiC whiskers. The fracture toughness is measured to be 5–7.7 MPa $m^{1/2}$ [9] for this type of materials, using Anstis' indentation method.

3.2. Thermal shock properties

Examples of the thermal shock behaviour at different quenching temperature differences (ΔT) for the whisker

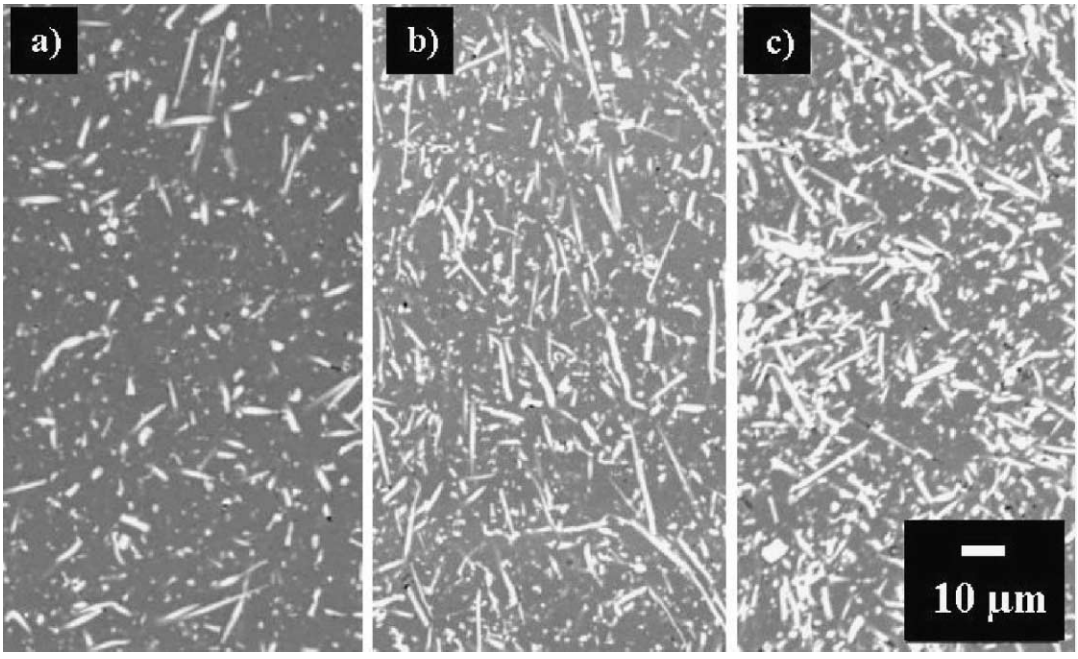

Fig. 1. SEM micrographs recorded in backscattered electron mode. Composites with (a) 10 vol.%, (b) 20 vol.% and (c) 40 vol.% Ti(C,N) whiskers. The reinforcing phase appears white and the matrix phase black or dark grey.

composites are given in Fig. 2. The thermal shock resistance increases with increasing amount of whiskers up to a volume fraction of 30%, where the optimum thermal shock properties are observed. A further increase in the volume fraction of whiskers leads to a decrease in the thermal shock resistance, see Fig. 3. The volume fraction of whiskers giving the best thermal shock resistance (30 vol.%) is also found in commercially available ceramic-cutting tools based on SiC-whisker reinforced alumina.

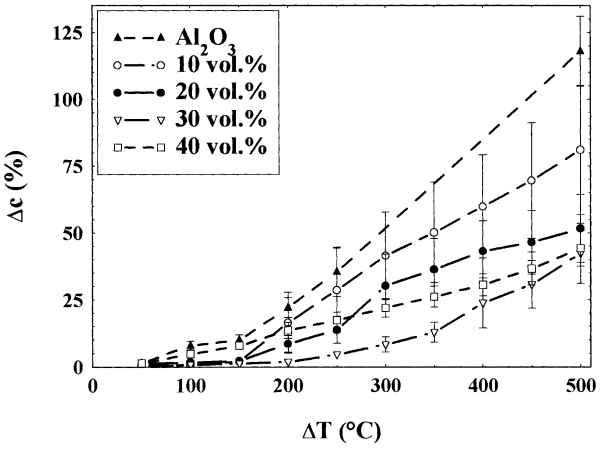

Fig. 2. Crack growth (Δc) versus temperature difference (ΔT) for representatives of the Ti(C,N) whisker composites.

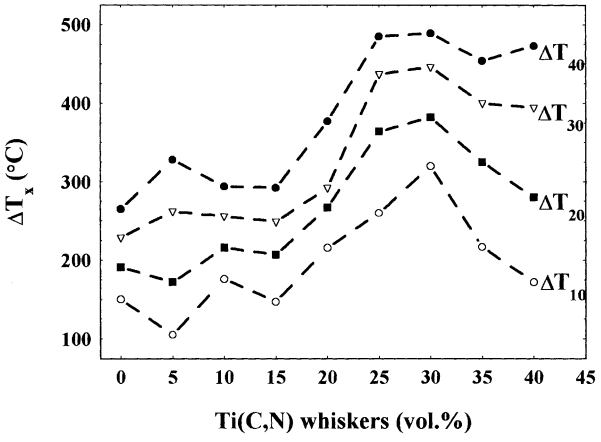

Fig. 3. Levels of different percentage of crack growth for the whisker reinforced composites. It is evident from the figure that the best thermal shock resistance is reached at a fraction of 30 vol.% whiskers.

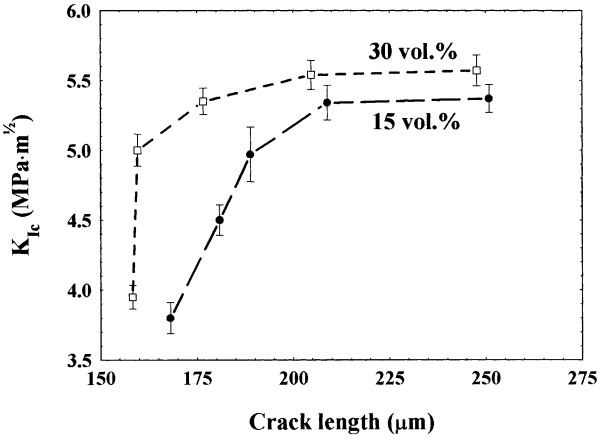

Fig. 4. The R-curve behaviour for two of the whisker composites.

The measurements show that the thermal shock resistance improves with increasing fracture toughness. Such a relation has also been observed for other brittle materials.[10] A clear R-curve behaviour is observed for the Ti(C,N) whisker-reinforced composites, see Fig. 4. Comparing the error bars in Fig. 2, it is clear that the scatter is largest at about 10 vol.% whiskers. This can be explained by that such a material have properties intermediate between pure alumina and a whisker-reinforced composite. With only 10 vol.% whiskers present, some of the cracks will grow solely in the alumina matrix, without meeting any whisker, while some cracks will meet whiskers that absorb crack energy and thus hinder the crack growth. There is thus wide scatter in crack growth for this type of material compared to materials containing a lower or higher fraction of whiskers. Increasing the volume fraction of whiskers above 10 vol.% leads to a continuously decreasing standard deviation in crack growth after thermal shock.

4. Conclusion

Alumina composites reinforced with different volume fractions of Ti(C,N) whiskers were produced to evaluate the thermal shock properties and to correlate the thermal shock resistance with the amount of reinforcing phase. An indentation–quench test was used for the thermal shock measurements.

The amount of Ti(C,N) whiskers was varied between 5 and 40 vol.% of the total composite volume. The indentation fracture toughness increased from 2.6 MPa $m^{1/2}$ for pure alumina to 5.0 MPa $m^{1/2}$ for the sample with 30 vol.% Ti(C,N) whiskers. The hardness also increased, from 17.6 to 24.2 GPa. The fracture toughness and the thermal shock resistance increases with increasing fraction of reinforcing phase up to 30 vol.% that was found to be the optimum volume fraction, so a clear correlation between the thermal shock resistance and the fracture toughness could be observed. The composites also show a clear R-curve behaviour.

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