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Alumina–chromium carbide composite through an internal synthesis method

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In situ formation of chromium carbide particles, through a solid state reaction between Cr_2O_3 and SiC, for strengthening Al_2O_3 has been studied. Three kinds of chromium compound, Cr_3Si, Cr_3C_2 and Cr_7C_3 and mullite were formed in the alumina matrix. The reaction behaviour during hot pressing depends on heating parameters such as temperature and atmosphere. In a vacuum environment, the Cr_3Si particles formed first and was the dominant dispersed phase below 1550 °C, while the Cr_7C_3 phase was only dominant above 1600 °C. The Cr_3C_2 phase emerged briefly then diminished at temperature $\geqslant$ 1500 °C. In an argon environment, however, the Cr_3C_2 phase was the main product component at temperatures ranging from 1450–1550 °C. The mullite phase formed concurrently through the diffusion of SiO_2 phase into the Al_2O_3 matrix, which is a by-product from the reaction between Cr_2O_3 and SiC. Incorporating chromium carbide or silicide particles into the Al_2O_3 matrix induces a strengthening effect. However, only when the content of dispersed phases is low and is mainly of Cr_3C_2 particles, is the strengthening effect significant. For instance, the composite, containing 5 vol% chromium carbide and hot-pressed at 1500 °C in argon, gives a flexural strength and fracture toughness up to 600 MPa and 6.1 MPa $m^{1/2}$, respectively.

1. Introduction

Using SiC whiskers to strengthen Al_2O_3 has been adopted for sometime and has been demonstrated to be quite effective [1, 2]. However, because of the health hazard, nowadays people are reluctant to handle whiskers.

A recent investigation [3] has demonstrated that addition of Cr_3C_2 particles is also an effective way of improving the mechanical properties of Al_2O_3. In addition, it makes the electric-discharge machining of sintered compacts possible. The problem is that Cr_3C_2 particles grow fairly fast during the sintering stage and the strengthening effect is obviously consequently reduced. Furthermore, the commercial Cr_3C_2 powder, which is available in the particle size range 3–7 μm, is not favourable for use as a starting material [4].

If the dispersed phase can be *in situ* formed in a ceramic matrix, the particle size can be much reduced by appropriately controlling the sintering temperature and time. Chromium carbide particles may be synthesized *in situ* through the reaction between Cr_2O_3 and SiC in an Al_2O_3 matrix [5]. Cr_2O_3 forms a solid solution with alumina at lower temperatures (< 1300 °C) and then diffuses out to react with SiC to form a chromium carbide phase at higher temperatures (> 1300 °C). In this way finer chromium carbide particles may be easily obtained. The chromium carbide is polymorphic, e.g. Cr_3C_2, Cr_7C_3 and $Cr_{23}C_7$, therefore some attention was paid to the phase transformation resulting from the temperature variation. On the other hand, it is expected that the mullite ($3Al_2O_3 \cdot 2SiO_2$) phase may occur due to the reaction between SiO_2, which is generated simultaneously with the carbide formation, and the Al_2O_3 matrix. Incorporating mullite into alumina brings an extra benefit in the lowering of the coefficient of thermal expansion (CTE) of the composite. This characteristic of mullite has been used to improve the spalling resistance of alumina refractories [6] and to increase the thermal shock resistance of hot-pressed alumina–molybdenum composite [7, 8].

The purpose of this work was to study the reaction between Cr_2O_3 and SiC in an alumina matrix and its effects on microstructure and mechanical properties of the composites.

2. Experimental procedure

The starting materials used for this investigation were SiC powder (average particle size ~ 2.58 μm, purity > 98 wt %), Cr_2O_3 powder (average particle size ~ 2.59 μm, purity > 99%) and Al_2O_3 powder (average particle size 0.3 μm, purity > 99%). Powders were mixed in a ball mill using ethanol as solvent. The

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mixing ratio for Cr_2O_3 to SiC was designed according to the stoichiometry of Cr_3C_2. Before sintering, the mixed powder was die-pressed at a pressure of 20 MPa to form discs of diameter 60 mm and thickness 5 mm. The discs were then hot-pressed in a graphite container at a constant pressure of 30 MPa and at various temperatures from 1100–1600 °C for 1 h in vacuum or an argon atmosphere. The sintered samples were examined by X-ray diffractometry (Phillips APD 1700 model) and optical microscopy after polishing with diamond paste of particle size down to 1 μm. Thin foils for TEM were prepared from thin slices cut using a high-speed diamond saw. These slices were ground to a thickness of ~ 60–80 μm. The final thinning was carried out by ion-beam milling with a 5 kV argon-ion beam incident on both surfaces of the foil at an angle of 12°. The thin foils were investigated using a Jeol 2000FX TEM.

The bulk density of sintered body was determined by Archimedes' method. The fracture strength, σ_f, was measured by the four-point bending method according to the JIS 1601 standard. The fracture toughness, K_{Ic}, was measured using the single-edge notched beam (SENB) method. Highly polished specimens were cut into 3 mm × 4 mm × 40 mm bars and these bars were centre-notched to one-third of their thickness using a 0.15 mm thick diamond blade. Both flexural strength and fracture toughness were measured at room temperature in a testing machine operated at a constant crosshead speed of 0.5 mm min^{-1}.

3. Results and discussion

3.1. Reactions between Cr_2O_3 and SiC

3.1.1. In vacuum

The X-ray diffraction (XRD) patterns of the specimens hot-pressed at 1100, 1300, 1500, 1550 and 1600 °C for 1 h are shown in Fig. 1. At 1100 °C, only peaks for Al_2O_3, Cr_2O_3, and SiC phase are apparent, indicating that no reaction occurred in the mixed powder. A clear Cr_3Si peak could be observed when the temperature was raised to 1300 °C, but a trace amount of Cr_2O_3 still retained unreacted. Formation of Cr_3Si phase implicitly suggests that the debonding of SiC may happen at a rather low temperature. This phenomenon can be supported by the experimental results from a previous work [9] showing that the highly polished SiC surface was roughened by annealing in vacuum. The debonded carbon reduces the chromia and frees silicon to react with chromium, forming Cr_3Si. This reaction may be represented by

$$3Cr_2O_3 + 2SiC + 3C \rightarrow 2Cr_3Si + CO\uparrow + 4CO_2\uparrow \qquad (1)$$

Excess carbon may be easily obtained because the specimens were placed in a graphite crucible. When the temperature was raised to 1500 °C, the Cr_3C_2 phase emerged and coexisted with Cr_3Si in the specimen. At 1550 °C, it is interesting to note that Cr_3C_2 phase is completely changed to Cr_7C_3, then Cr_3Si and Cr_7C_3 become the coexisting phases. Although the Cr_3Si phase exists at temperatures from 1300–1550 °C, however, it cannot exist at temperatures higher than 1550 °C. At temperatures ≥ 1600 °C, Cr_7C_3 is the only phase observed. The phases formed at different temperatures in a vacuum and an argon atmosphere are summarized in Table I, in which phase content is listed in terms of the ratio of the main XRD peak intensity. The phase transformation of chromium carbide in vacuum may arise as follows. After debonding of SiC, some carbon reacted with chromia to generate CO and CO_2 gases. These gases were continuously pumped out of the vacuum system, whereas they accumulated and were retained in the argon system. Based on the thermodynamic equilibrium point of view, continuous removal of CO and CO_2 will favour the reaction (1) towards the right. This means that in a vacuum system the Cr_3Si phase is the most favourable species to form. This is exactly the phenomenon that has been observed in the experiment.

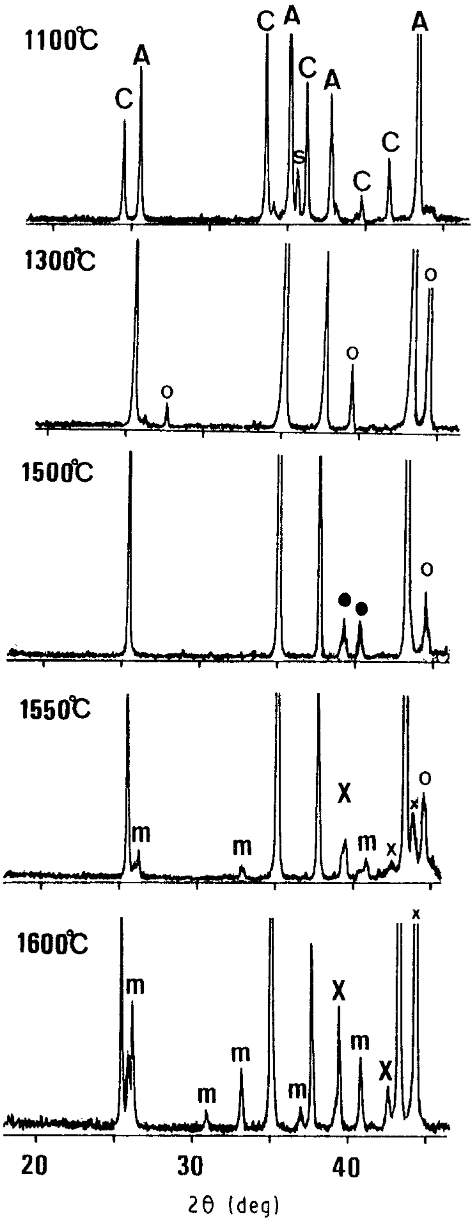

Figure 1 XRD patterns of the samples hot-pressed at 1100, 1300, 1500, 1550 and 1600 °C for 1 h in vacuum. A, Al_2O_3; m, mullite; (○) Cr_3Si; (×) Cr_7C_3; (●) Cr_3C_2; S, SiC; C, Cr_2O_3.

TABLE I The intensity ratio of main XRD peak of different phases at various temperatures in a vacuum or an argon atmosphere

Temperature (°C)	Atmosphere	Phase[a]	Intensity ratio
1300	Ar	Cr_3Si	
1300	Vacuum	Cr_3Si	
1400	Ar	Cr_3Si, Cr_7C_3, Cr_3C_2	1:3:1.5
1450	Ar	Cr_3C_2	
1500	Ar	Cr_7C_3, Cr_3C_2	1:4.5
1500	Vacuum	Cr_3Si, Cr_3C_2	1:0.5
1550	Ar	Cr_7C_3, Cr_3C_2	1:1
1550	Vacuum	Cr_3Si, Cr_7C_3	1:0.7
1600	Ar	Cr_7C_3	
1600	Vacuum	Cr_7C_3	

[a] In addition to Cr_3Si, Cr_7C_3, Cr_3C_2, another two phases are Al_2O_3 and mullite.

3.1.2. *In an argon atmosphere*

Fig. 2 shows the XRD patterns of the specimens hot-pressed at 1300, 1400, 1450, 1500, 1550 and 1600 °C for 1 h. Again, the Cr_3Si phase was formed first at 1300 °C, and rapidly diminished at 1450 °C. At 1400 °C, Cr_3C_2 and Cr_7C_3 could coexist with the Cr_3Si.

The difference between argon and vacuum conditions is that the Cr_3C_2 phase dominates in the reactants in temperature range 1450–1550 °C in the argon system, but in a vacuum only a small amount of Cr_3C_2 can be found at 1500 °C and Cr_3C_2 began to change to Cr_7C_3 at 1550 °C. At temperatures $\geqslant 1600$ °C and in argon, the Cr_3C_2 phase is completely transformed to Cr_7C_3.

The mechanisms for the abrupt phase transformation of chromium carbide from Cr_3C_2 to Cr_7C_3 between 1500 and 1550 °C and the disappearance of Cr_3Si at 1450 °C, need further investigation.

The replacement of some of the Al_2O_3 matrix by mullite, which originated from the reaction between free SiO_2 and Al_2O_3, can be represented by

$$3Cr_2O_3 + 4SiC + C \rightarrow 2Cr_3C_2 + 4SiO_2 + CO\uparrow \quad (2)$$

$$2SiO_2 + 3Al_2O_3 \rightarrow 3Al_2O_3\cdot 2SiO_2 \text{ (mullite)} \quad (3)$$

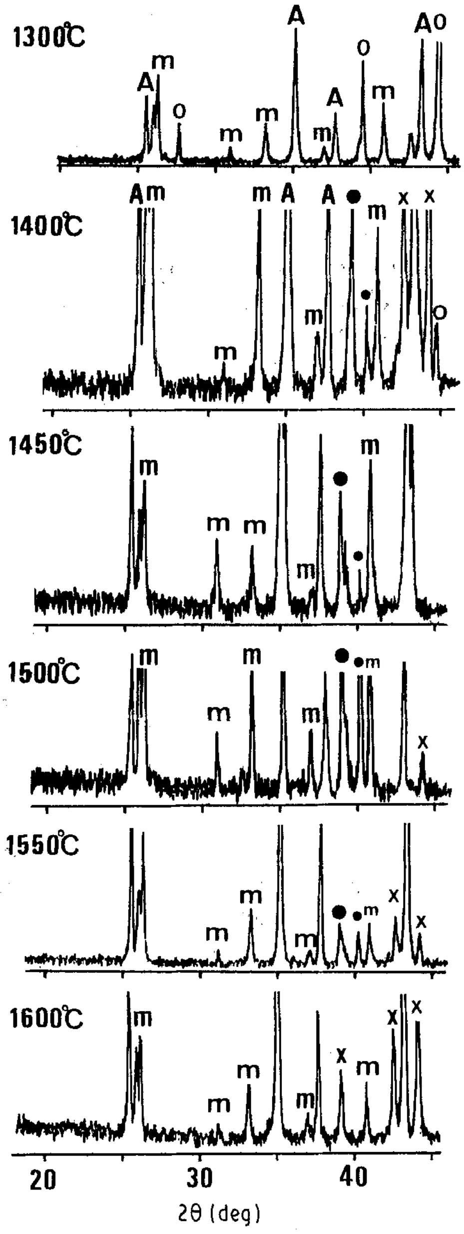

Figure 2 XRD patterns of the samples hot-pressed at 1300, 1400, 1450, 1500, 1550 and 1600 °C for 1 h in an argon atmosphere. A, Al_2O_3; m, mullite; (○) Cr_3Si; (×) Cr_7C_3; (●) Cr_3C_2.

3.2. Microstructure development

Fig. 3 shows an optical micrograph of synthesized chromium carbide particles (white) obtained by using hot-pressing at 1450 °C in argon. The chromium carbide particles were well dispersed in the Al_2O_3 matrix. Figs 4 and 5 show transmission electron micrographs and selected-area diffraction patterns (SADP) of the composites with 5 vol % chromium carbide, which were sintered at 1450 and 1500 °C in argon, respectively. The precipitated phases were identified as being consistent with the XRD results, i.e. only Cr_3C_2 exists at 1450 °C, while Cr_3C_2 and Cr_7C_3 coexist at 1500 °C. Cr_3C_2 has an orthorhombic structure (Fig. 4b), but Cr_7C_3 exists as a hexagonal structure (Fig. 5b). A large number of chromium carbide particles precipitated in

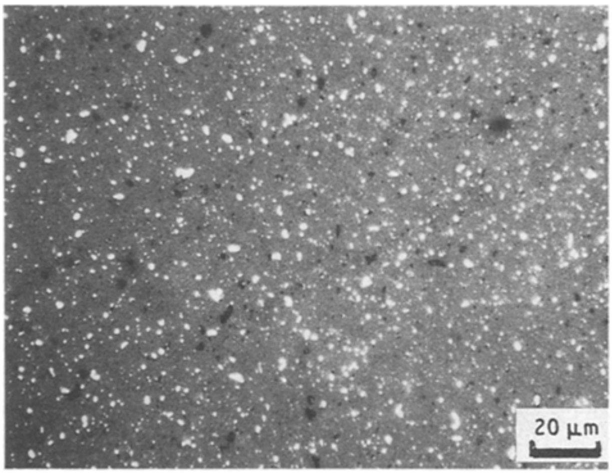

Figure 3 Optical photograph of the composite containing 10 vol % chromium carbide. The composite was obtained by hot pressing at 1450 °C in argon.

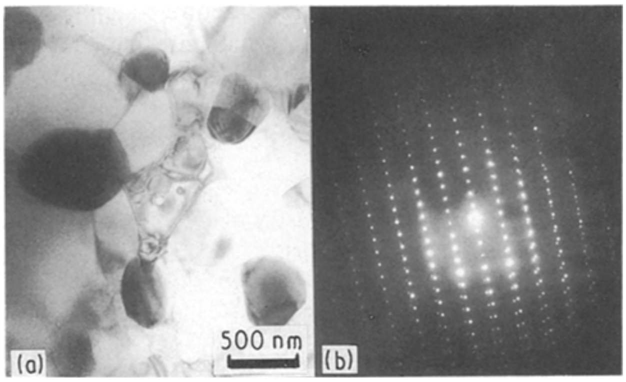

Figure 4 Transmission electron micrographs of the composite containing 5 vol % chromium carbide and hot-pressed at 1450 °C in argon, showing (a) bright-field image, (b) selected-area diffraction pattern (SADP) of Cr_3C_2 with zone axis $[1\,0\,\bar{1}]$.

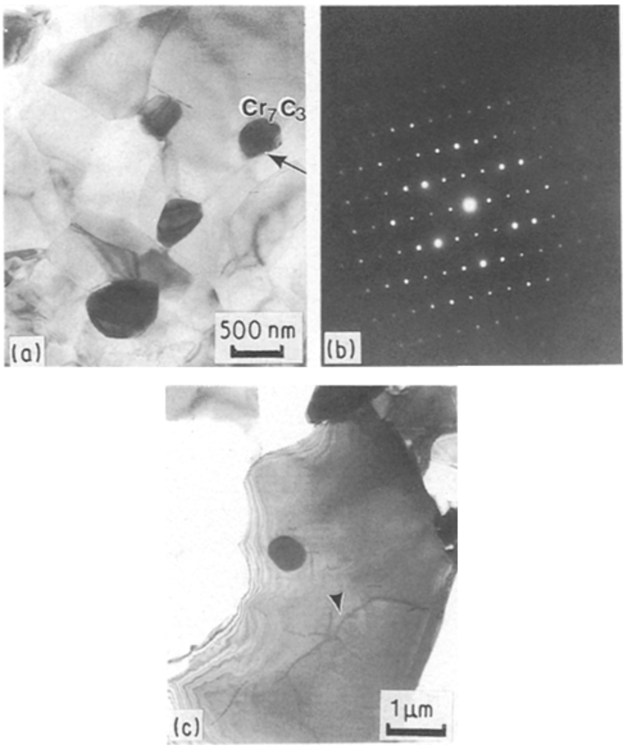

Figure 5 Transmission electron micrographs of the composite containing 5 vol % chromium carbide and hot-pressed at 1500 °C in argon, showing (a) bright-field image, (b) SADP of Cr_7C_3 phase of hexagonal structure with zone axis $[\bar{1}\,1\,0]$, (c) appearance of dislocation in the matrix (arrowed).

the intragrains of the matrix; this induced the appearance of dislocations in the matrix (see Fig. 5c). It is not possible to distinguish the Al_2O_3 matrix from the mullite in the transmission electron micrograph. The chromium carbide particle size is estimated to be from 0.1–1.5 μm, which is much smaller than the commercially available Cr_3C_2 powder, as expected.

3.3. Mechanical properties

Figs 6 and 7 show the variation of flexural strength and fracture toughness as a function of added chromium carbide content for the composites hot-

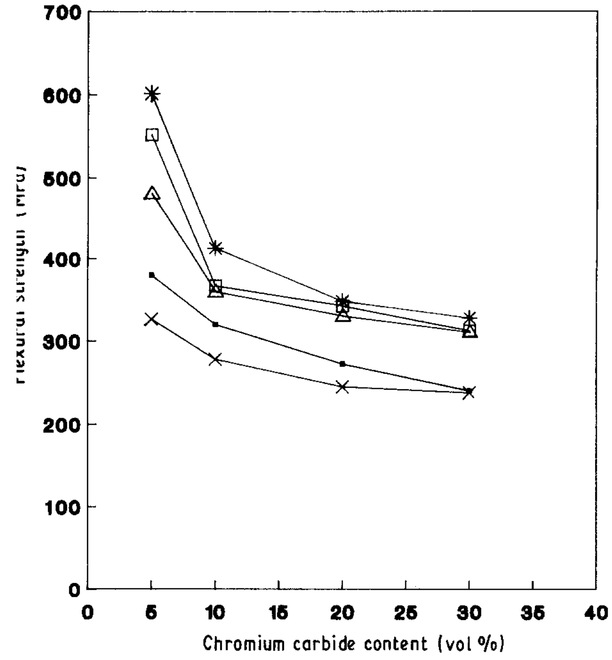

Figure 6 Variation of flexural strength as a function of added chromium carbide content for the composites hot-pressed at various temperatures in argon. (■) 1600 °C, (△) 1550 °C, (∗) 1500 °C, (□) 1450 °C, (×) 1400 °C.

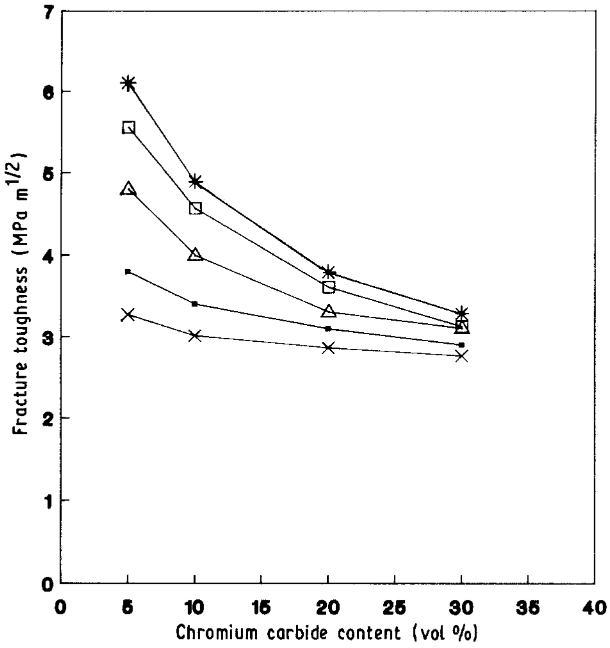

Figure 7 Variation of fracture toughness as a function of added chromium carbide content for the composites hot-pressed at various temperatures. For key, see Fig. 6.

pressed at various temperatures in argon. Densification of specimens in excess of 99% theoretical density (TD) was achieved. The flexural strength and fracture toughness decreased drastically as the dispersed phase content was increased. The decrease in the strength and toughness is thought to be due to an increasing amount of Al_2O_3 matrix being replaced by mullite. A similar case was also reported for alumina–mullite ceramics for multilayer substrates [10]. Within the sintering temperature range 1450–1500 °C, Cr_3C_2 is the dominant phase which has better mechanical properties than Cr_7C_3 and Cr_3Si. This induces in the composites, better mechanical properties for those sintered at the temperature range 1450–1500 °C. The composite containing 5 vol % chromium carbide, which was sintered at 1500 °C in argon, can give a flexural strength and fracture toughness up to 600 MPa and 6.1 MPa $m^{1/2}$, respectively.

4. Conclusions

1. *In situ* formation of chromium carbide particles through the internal synthesis method was thoroughly investigated. The phase transition behaviour is summarized as follows.

(a) In a vacuum system, Cr_3Si is the first phase formed, emerging at 1300 °C, and remains the dominant phase up to 1550 °C. Cr_3C_2 phase can only be observed between 1500 and 1550 °C. If the temperature is higher than 1550 °C, all Cr_3C_2 phase is transformed to Cr_7C_3.

(b) In an argon atmosphere, Cr_3C_2 phase coexists with Cr_7C_3 phase at temperatures from 1400–1550 °C, and Cr_3C_2 is dominant between 1450 and 1550 °C. This indicates that an argon atmosphere is more favourable for chromium carbide formation, than is a vacuum.

(c) At temperatures $\geqslant 1600$ °C, Cr_7C_3 is the only phase observed either in a vacuum or in an argon atmosphere.

2. The average particle size of chromium carbide, obtained through the internal synthesis method, ranges from 0.1–1.5 μm, which is much smaller than that of the starting powder.

3. For the composite containing 5 vol % chromium carbide, and hot-pressed at 1500 °C in argon, a flexural strength of 600 MPa and fracture toughness of 6.1 MPa $m^{1/2}$, are obtained, which are superior to those of monolithic Al_2O_3.

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