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# An internal synthesis method for mullite–chromium carbide composite in a vacuum system

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*In situ* formation of chromium carbide in a mullite matrix through reaction of $Cr_2O_3$, SiC and $Al_2O_3$ has been studied. Three different chromium compounds, $Cr_3Si$, $Cr_3C_2$, $Cr_7C_3$, and mullite were formed. In a vacuum environment, the $Cr_3Si$ particles formed first and were retained below 1550 °C, while the $Cr_7C_3$ phase was only dominant above 1600 °C. The $Cr_3C_2$ phase was the dominant dispersed phase at temperatures of 1450–1500 °C. In an argon environment, the $Cr_3C_2$ phase was the main product component at temperatures ranging from 1450 to 1550 °C. The mullite phase formed concurrently through the diffusion of the $SiO_2$ phase into the $Al_2O_3$. $SiO_2$ was the product of the reaction between $Cr_2O_3$ and SiC. The composite hot-pressed at 1450 °C in vacuum gave a flexural strength and fracture toughness of up to 457 MPa and 4.1 MPa $m^{1/2}$, respectively.

## 1. Introduction

Mullite is an attractive material for certain structural applications because of its excellent creep resistance, low thermal expansion coefficient, better thermal shock resistance and high temperature strength retention. However, mullite suffers from low strength and low fracture toughness. The use of SiC whiskers and zirconia to strengthen mullite has been adopted for sometime and has been demonstrated to be quite effective [1–4].

A recent investigation has demonstrated that the addition of $Cr_3C_2$ particles is also an effective way of improving the mechanical properties of $Al_2O_3$ [5]. In addition, it makes electric–discharge machining of sintered compacts possible. The problem is that $Cr_3C_2$ particles grow fairly quickly during the sintering stage, and the strengthening effect is, obviously, consequently reduced. Furthermore, commercial $Cr_3C_2$ powder, which is available in a particle size range of 3–7 μm, is not favourable for use as a starting material [6].

If the dispersed phase can be formed *in situ* 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 reaction between $Cr_2O_3$ and SiC in an $Al_2O_3$ matrix [7, 8]. $Cr_2O_3$ 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. There are several chromium carbides, e.g. $Cr_3C_2$, $Cr_7C_3$ and $Cr_{23}C_7$, therefore, attention was paid to the formation of these compounds resulting from temperature variation. On the other hand, it is expected that the mullite ($3Al_2O_3 \cdot 2SiO_2$) phase may occur due to reaction between $SiO_2$, which is generated simultaneously with carbide formation, and $Al_2O_3$.

In previous work [9], reaction among $Cr_2O_3$, SiC and $Al_2O_3$ in an argon atmosphere seems to inhibit densification of the composites. The purpose of this work was to study the reaction in vacuum, and compare its effects on microstructural and mechanical properties of the composites with effects in an argon atmosphere.

## 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 a solvent. The $Cr_2O_3$:SiC mixing ratio was designed according to the stoichiometry of $Cr_3C_2$ and mullite ($3Al_2O_3 \cdot 2SiO_2$). Before sintering, the mixed powder was die-pressed at a pressure of 20 MPa to form discs of 60 mm diameter and 5 mm thickness. 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 in an argon atmosphere. The sintered samples were examined by X-ray diffractometry (Phillips APD 1700 model), electron spectroscopy for chemical analysis (ESCA) and optical microscopy after polishing with a diamond paste of particle size down to 1 μm. Thin foils for transmission electron microscopy

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(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 LINK EDAX energy dispersive X-ray spectrometer (EDS) attachment.

The phase composition of the sintered samples was determined by X-ray quantitative analysis and chemical analysis. The bulk density of the sintered body was determined by Archimedes' method. The flexural strength, $\sigma_f$, was measured by the four-point bending method according to the JIS 1601 standard, the fracture toughness, $K_{1c}$, was measured using the single-edge notched beam (SENB) method. Highly polished specimens were cut into 3 × 4 × 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 $\text{min}^{-1}$. Each data point was the average of at least five tests.

## 3. Results and discussion

### 3.1. Reaction among $Cr_2O_3$, SiC and $Al_2O_3$ and phase identification

The X-ray diffraction (XRD) patterns of the specimens hot-pressed at 1100, 1300, 1400, 1450, 1500 and 1600 °C for 1 h in vacuum are shown in Fig. 1. At 1100 °C, only peaks for $Al_2O_3$, $Cr_2O_3$ and SiC phases 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 $Cr_2O_3$ was still retained unreacted. Formation of $Cr_3Si$ phase implicitly suggests that debonding of SiC may happen at rather low temperatures. This phenomenon can be supported by experimental results from a previous work [10] showing that the highly polished SiC surface was roughened by annealing in vacuum at 1200 °C. The debonded carbon reduces chromia and frees silicon to react with chromium, forming $Cr_3Si$. This reaction may be represented by

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

Excess carbon may be easily obtained because the specimens were placed in a graphite crucible.

At 1400 °C, $Cr_3C_2$ and $Cr_7C_3$ could coexist with $Cr_3Si$. The $Cr_3C_2$ phase dominates in the reactants at temperatures ranging from 1450 to 1500 °C; but a small amount of $Cr_3Si$ was still present. At 1550 °C, it is interesting to note that the $Cr_3C_2$ 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 to 1550 °C, however, it cannot exist at temperatures higher than 1550 °C. At temperatures ≥ 1600 °C, $Cr_7C_3$ is the only phase observed. Fig. 2 shows the XRD patterns

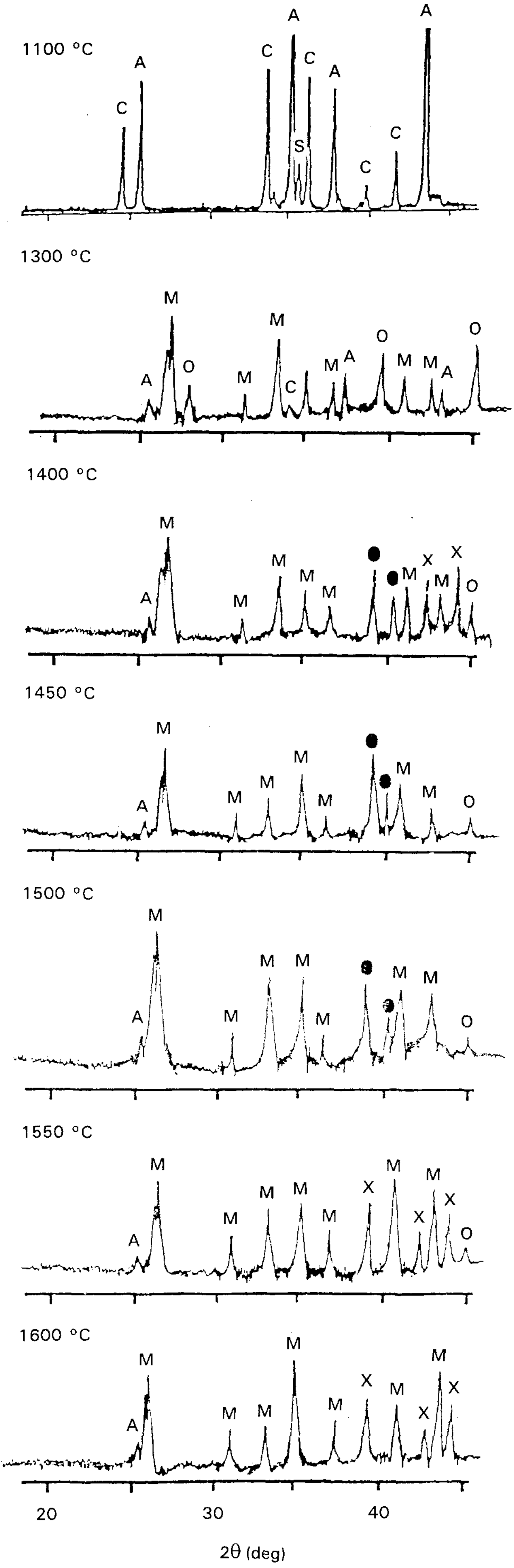

*Figure 1* XRD patterns of samples hot-pressed at 1100, 1300, 1400, 1450, 1500, 1550 and 1600 °C for 1 h in vacuum: (A) $Al_2O_3$, (M) Mullite, (O) $Cr_3Si$, (X) $Cr_7C_3$, (●) $Cr_3C_2$, (C) $Cr_2O_3$, and (S) SiC.

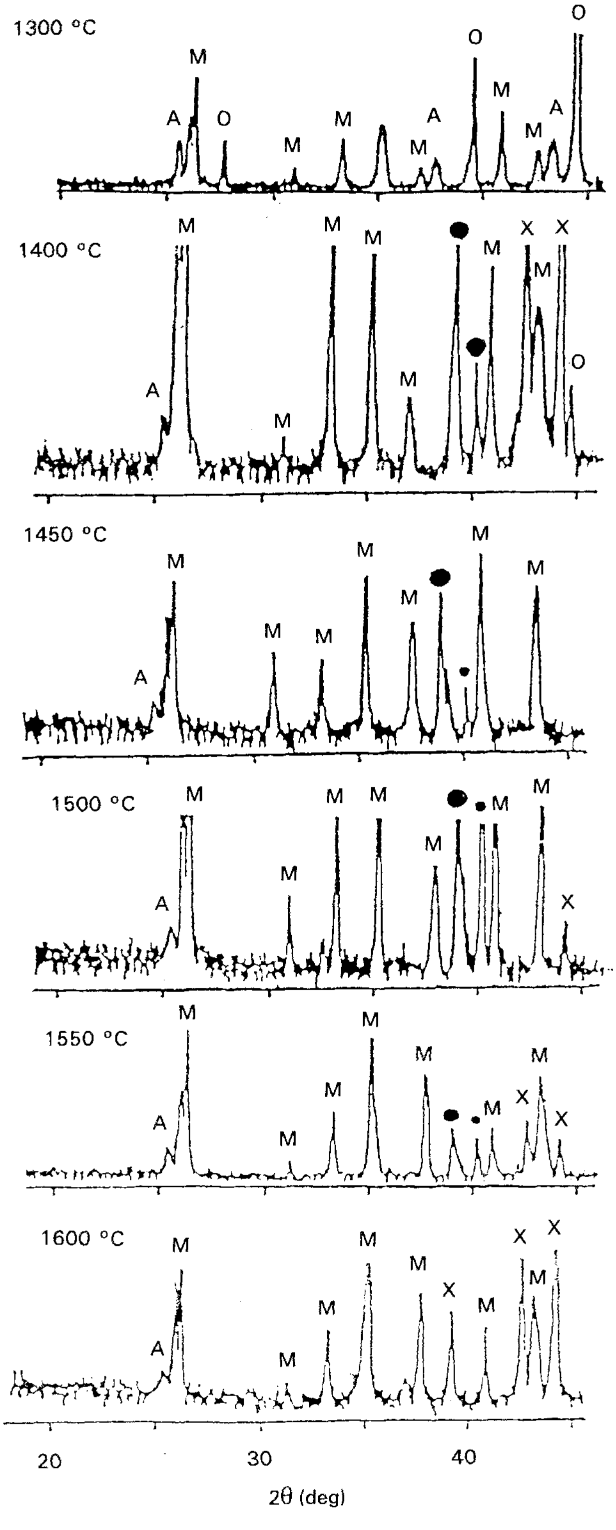

*Figure 2* XRD patterns of samples hot-pressed at 1300, 1400, 1450, 1500, 1550 and 1600 °C for 1 h in an argon atmosphere: (A) $Al_2O_3$, (M) Mullite, (O) $Cr_3Si$, (X) $Cr_7C_3$, (●) $Cr_3C_2$, (C) $Cr_2O_3$, and (S) SiC.

of the specimens hot-pressed at 1300, 1400, 1450, 1500, 1550 and 1600 °C for 1 h [9]. 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 $Cr_3Si$.

The difference between argon and vacuum conditions is that the $Cr_3C_2$ phase dominates in the reactants in the temperature range of 1450–1550 °C in the argon system, but in a vacuum the $Cr_3C_2$ phase is the main component at 1450–1500 °C, and $Cr_3C_2$ began to change to $Cr_7C_3$ at 1550 °C. At temperatures $\geq$ 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 and 1600 °C, need further investigation.

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

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

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

Substantial mullite formation at temperatures above 1400 °C was confirmed by XRD in Figs 1 and 2, but a small amount of alumina was retained in the sample.

### 3.2. Density

The density of the sintered body was measured after sintering. The relative densities and 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 volume fraction. The volume fraction of $SiO_2$ was determined from the remaining $Al_2O_3$ and $Cr_3Si$. The relative densities of the composites sintered in an argon atmosphere are all approximate to 98% [9], but the composites can be densified up to 99%, theoretical density, if sintering is in a vacuum atmosphere. The higher density in vacuum may arise as follows. Reaction during sintering may 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. These gases are detrimental to densification of the composites. This indicates that it is crucial in the pumping out of CO and $CO_2$ gases.

### 3.3. Microstructure development

Fig. 3 shows an optical micrograph of synthesized chromium carbide particles (white) obtained by hot-pressing at 1450 °C in vacuum. The chromium carbide particles were well dispersed in the mullite matrix. Figs 4, 5 and 6 show transmission electron micrographs and selected-area diffraction patterns (SADP) of the composites, which were sintered at 1450 °C in vacuum or in argon, 1550 °C in vacuum, and 1600 °C in an argon atmosphere, respectively. The precipitated phases were identified as being consistent with the XRD results, i.e. $Cr_3C_2$ exists at 1450 °C, while only $Cr_7C_3$ exists at 1550 °C in vacuum. $Cr_3C_2$ has an orthorhombic structure (Fig. 4c), but $Cr_7C_3$ exists as a hexagonal structure (Fig. 5b). A large number of chromium carbide particles precipitated in the intragrains of the matrix, this induced the appearance of dislocations and strain contour in the matrix (see Fig. 4b). The intragranular chromium carbide which is

TABLE I The relative densities and different phases at various temperatures in a vacuum or argon atmosphere

| Temperature (°C) | Atmosphere | Phase[a] | Volume ratio | Relative density (%) |
|---|---|---|---|---|
| 1300 | Argon | $Cr_3Si$ | | |
| 1300 | Vacuum | $Cr_3Si$ | | |
| 1400 | Argon | $Cr_3Si$, $Cr_7C_3$, $Cr_3C_2$ | 1:3:1.5 | 97.7 |
| 1400 | Vacuum | $Cr_3Si$, $Cr_7C_3$, $Cr_3C_2$ | 1:2:1.6 | 98.6 |
| 1450 | Argon | $Cr_3C_2$ | | 98.1 |
| 1450 | Vacuum | $Cr_3Si$, $Cr_3C_2$ | 1:7.5 | 98.9 |
| 1500 | Argon | $Cr_7C_3$, $Cr_3C_2$ | 1:4.5 | 98.2 |
| 1500 | Vacuum | $Cr_3Si$, $Cr_3C_2$ | 1:7.6 | 98.9 |
| 1550 | Argon | $Cr_7C_3$, $Cr_3C_2$ | 1:1 | 98.2 |
| 1550 | Vacuum | $Cr_3Si$, $Cr_7C_3$ | 1:5.8 | 99.1 |
| 1600 | Argon | $Cr_7C_3$ | | 98.3 |
| 1600 | Vacuum | $Cr_7C_3$ | | 99.2 |

[a] Except for $Cr_3Si$, $Cr_7C_3$, $Cr_3C_2$, the other three phases are mullite, $Al_2O_3$ and $SiO_2$.

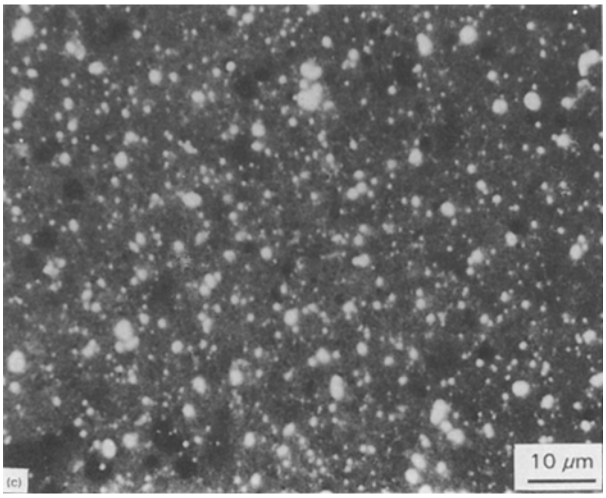

*Figure 3* Optical photograph of the composite obtained by hot-pressing at 1450 °C in vacuum.

enclosed in mullite grains is generally round and very small. The intergranular chromium carbide has a larger mean particle size and sharp-edged grains, which are located at mullite grain boundaries or partly inside the mullite and at the boundaries. By using EDS microanalysis on the position marked with an arrow in Fig. 6, it is shown that there is a significant amount of $SiO_2$ remaining in the grain boundaries of mullite, forming a glassy phase. The chromium carbide particle size is estimated to be ~ 0.1–1.5 μm, which is much smaller than the commercially available $Cr_3C_2$ powder, as expected.

### 3.4. Mechanical properties

Figs 7 and 8 show the variation of flexural strength and fracture toughness as a function of hot-pressing temperatures in vacuum or in an argon atmosphere. The error bars in Figs 7 and 8 indicate the standard deviation of measured values. The flexural strength of the composite sintered at 1450 °C was up to 457 MPa in vacuum and 407 MPa in an argon atmosphere [9]. The fracture toughness of the composite sintered at 1450 °C was 4.1 MPa $m^{1/2}$ in vacuum and 3.8 MPa $m^{1/2}$ in an argon atmosphere [9]. The lower flexural strength and fracture toughness in the composites sintered in argon, compared with those sintered in vacuum conditions, may be due to the low relative density as shown in Table 1.

Within the sintering temperature range, 1450–1500 °C, $Cr_3C_2$ is the dominant phase, and has better mechanical properties than $Cr_7C_3$ and $Cr_3Si$. This induces in the composites, better mechanical

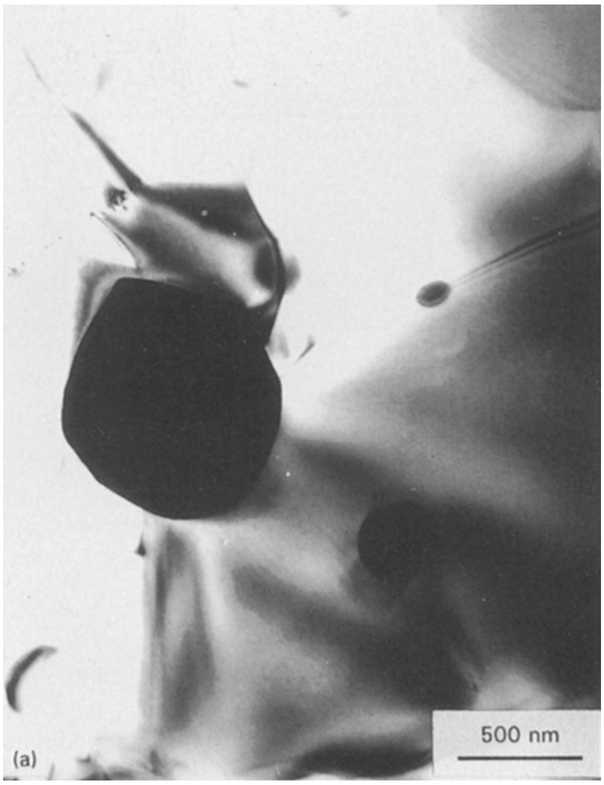

*Figure 4* TEM micrographs of the composite hot-pressed at 1450 °C (a) in vacuum; (b) in argon, showing bright field image and appearance of dislocation, strain contour in the matrix; and (c) selected-area diffraction pattern (SADP) of $Cr_3C_2$ phase with orthorhombic structure with zone axis $[10\bar{1}]$.

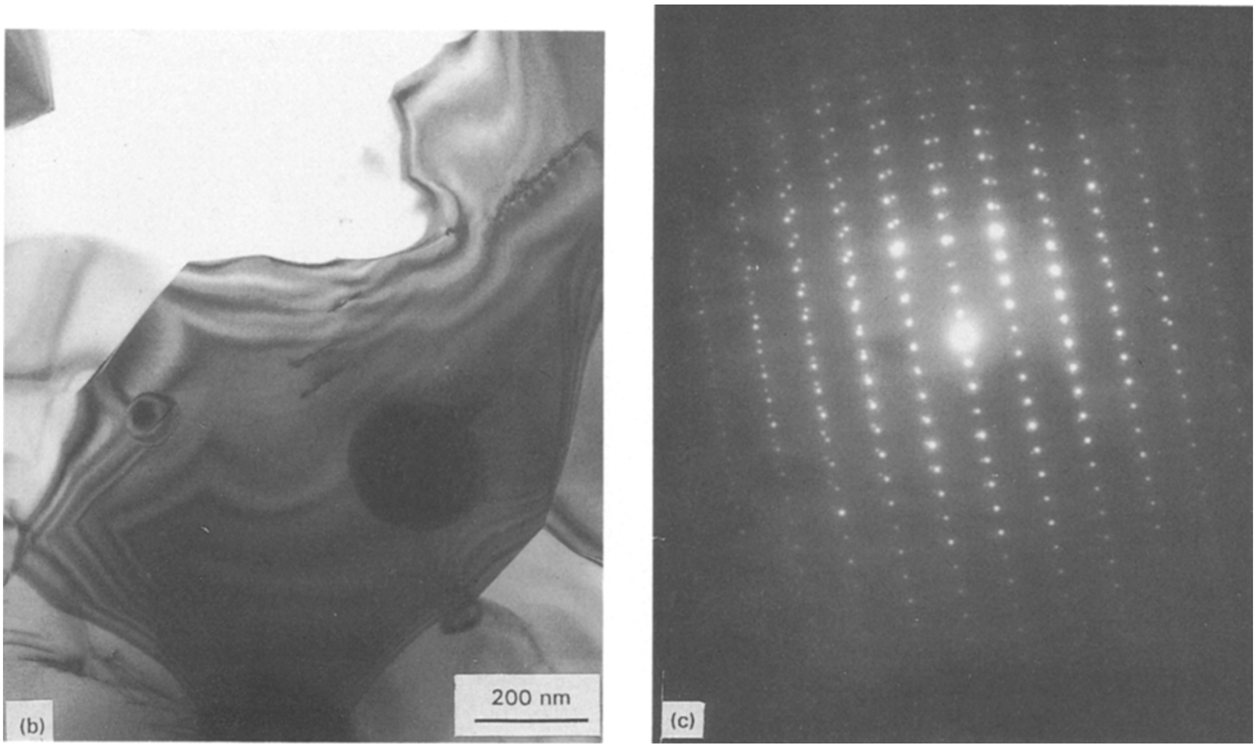

*Figure 4* *Continued.*

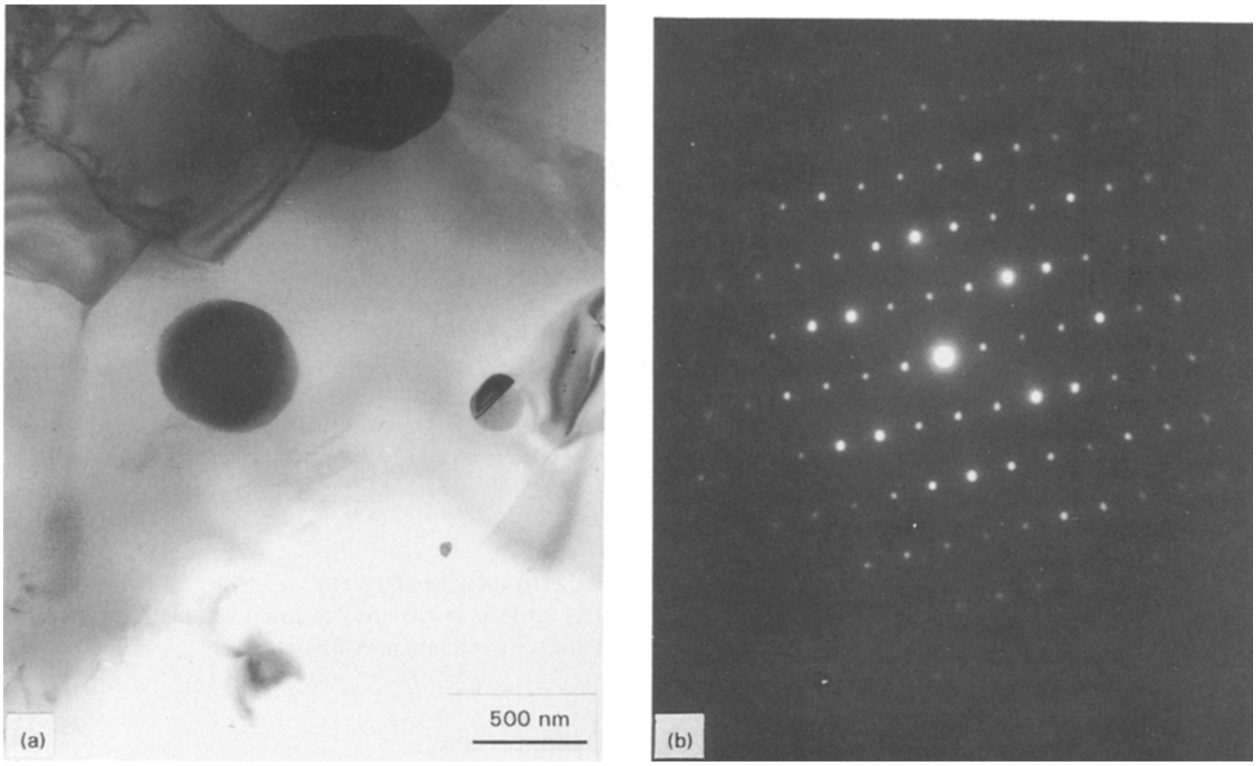

*Figure 5* TEM micrographs of the composite hot-pressed at 1550 °C in vacuum, showing (a) bright field image, and (b) SADP of $Cr_7C_3$ phase with hexagonal structure with zone axis $[\bar{1}10]$.

properties for those sintered in the temperature range of 1450–1500 °C.

## 4. Conclusions

1. *In situ* formation of mullite-containing chromium carbide particle composites through the internal synthesis method was investigated. The following carbide phases were observed after hot-pressing.

(a) In a vacuum system, $Cr_3Si$ was the first phase formed, emerging at 1300 °C, and remained up to 1550 °C. The $Cr_3C_2$ phase was dominant between

*Figure 6* TEM micrograph of the composite hot-pressed at 1600 °C in argon, showing an amount of $SiO_2$ left in grain boundaries of mullite.

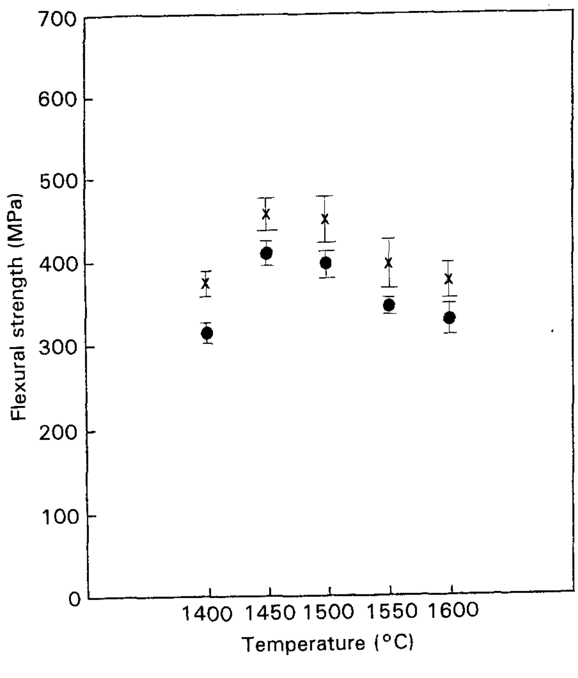

*Figure 7* Variation of flexural strength as a function of hot-pressing temperature for the composites: (●) in argon, (X) in vacuum.

1450–1550 °C. If the temperature is higher than 1550 °C, all the $Cr_3C_2$ phase is transformed to $Cr_7C_3$.

(b) In an argon atmosphere, the $Cr_3C_2$ phase coexisted with the $Cr_7C_3$ phase at temperatures ranging from 1400 to 1550 °C, and $Cr_3C_2$ was dominant between 1450–1550 °C.

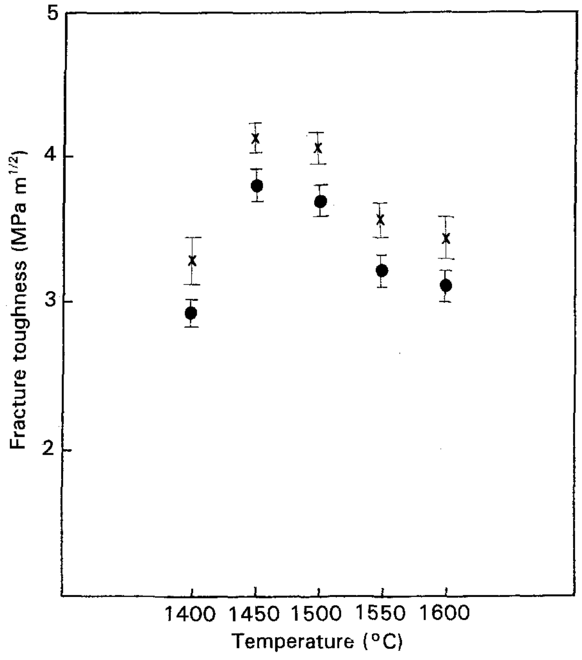

*Figure 8* Variation of fracture toughness as a function of hot-pressing temperature for the composites: (●) in argon, (X) in vacuum.

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

(d) The sample sintered above 1400 °C was mostly mullite in addition to $Cr_3Si$, $Cr_7C_3$ and $Cr_3C_2$, but a small amount of $Al_2O_3$ was retained.

2. The average particle size of chromium carbide, obtained by 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 hot-pressed at 1450 °C in argon, a flexural strength of 407 MPa and a fracture toughness of 3.8 $\mathrm{MPa\,m^{1/2}}$ are obtained. For the composite hot-pressed at 1450 °C in vacuum, which shows the best performance in the mechanical test, a flexural strength of 457 MPa and a fracture toughness of 4.1 $\mathrm{MPa\,m^{1/2}}$ are observed.

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