Microstructure and mechanical properties of Cr$_3$C$_2$ particulate reinforced Al$_2$O$_3$ matrix composites

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Al$_2$O$_3$ matrix with three grades of Cr$_3$C$_2$ particle size (0.5, 1.5 and 7.5 µm) composites were fabricated by a hot-pressing technique. Fully dense compacts with Cr$_3$C$_2$ content up to 40 vol% can be acquired at 1400 °C under 30 MPa pressure for 1 h. The flexural strength increases from 595 to 785 MPa for fine Cr$_3$C$_2$ particle (0.5 µm) reinforced Al$_2$O$_3$ matrix composites. The fracture strength is significantly dependent on the fracture modes of matrix (intergranular or transgranular). The transgranular fracture with a compressive residual stress gives a high fracture strength of composites. At the same time, the fracture toughness increases from 5.2 MPa m$^{1/2}$ (10 vol% Cr$_3$C$_2$) to 8.0 MPa m$^{1/2}$ (30 vol% Cr$_3$C$_2$) for the coarse Cr$_3$C$_2$ particle (7.5 µm) reinforced Al$_2$O$_3$ matrix composites. The toughening effects of incorporating Cr$_3$C$_2$ particles into Al$_2$O$_3$ matrix originate from crack bridging and deflection. The electrical conductivity and the possibility of electrical discharge machining of these composites were also investigated.

1. Introduction
Monolithic alumina is one of the most popular ceramic materials used in wear and structural applications, based on its excellent physical properties such as high melting temperature, strength, hardness and corrosion resistance. However, the intrinsic brittleness of alumina makes its reliability limited and prevents wider usage. Various remedies have been employed to increase its toughness, including the use of hard ceramic particulate as a reinforcing phase, which has been shown to be very effective in strengthening and toughening alumina [1–4].

Recently, there has been progress in the development of electroconductive ceramic materials [5–7]. These electroconductive and toughened ceramics could be shaped by electrical discharge machining to manufacture complex components, instead of using expensive conventional diamond tools. In order to obtain such ceramics, an electroconductive phase must be dispersed in an insulated ceramic matrix. With the addition of low electrical resistivity (< $10^{-5}$ Ω cm) transition metal carbides, borides or nitrides (e.g. TiC, TiN or TiB$_2$) to improve the electroconductivities of non-oxides [5,6] or Al$_2$O$_3$ [6,7] matrix, good electroconductive ceramic composites have been demonstrated. At the same time, these composites could be used as high-temperature heaters, igniters and so on to extend the applications, in addition to the wear-resistant components and cutting tools.

In addition to the high modulus and electrical conductivity, the Cr$_3$C$_2$ constituents possess outstanding high-temperature erosion resistance, at least to 1100 °C, which makes the materials ideally suitable for hot extrusion dies [8]. In this study, the correlations between densification, microstructures, mechanical properties and electrical conductivity of Al$_2$O$_3$ matrix composites with the incorporation of ~ 10–40 vol % Cr$_3$C$_2$ particles are investigated. The preliminary results of the size effects of Cr$_3$C$_2$ particles on microstructures and mechanical properties are also discussed.

2. Experimental procedures
2.1. Raw materials
The Cr$_3$C$_2$ powder used was from Herman C. Stark, with a purity of > 99%. Three sizes of Cr$_3$C$_2$ particle were used. The mean particle sizes measured by laser diffraction techniques were 7.5 (L), 1.5 (M) and 0.5 µm (S), respectively. The finest particle was obtained by attritor-milled 1.5-µm particle for 48 h. The Al$_2$O$_3$ powder (Alcoa A16-SG) had a particle size of 0.3–0.5 µm and purity of > 99.7%.
2.2. Consolidation procedures
The Cr$_3$C$_2$ and Al$_2$O$_3$ powders were added together and deionized water and then ball-milled for 24 h. The slurry was further homogenized for 15 min using a high-shear ultrasonic dispersing process. The homogenized slurry was dried rapidly with constant agitation on a hot plate. The dried and sieved mixture was uniaxially pre-pressed to form discs of 5 mm in height and 60 mm in diameter. The green compacts were then placed in a boron nitride-coated graphite mould and hot pressed in the temperature range 1200 to 1700°C in Ar atmosphere, at a pressure of 30 MPa for 1 h.

2.3. Characterization
The dense composite discs were ground and cut along the grinding direction to $3 \times 4 \times 40$-mm bars. All specimens were polished with diamond pastes from 15 down to 3 μm. Each bar to be used for the fracture toughness test was centre-notched to one-third of its thickness using a 0.15-mm-thick diamond blade. The flexural strength was measured through a four-point bending test following the JIS 1601 method [9] and the fracture toughness was evaluated using the single-edge-notched beam (SENB) method. Both were measured at room temperature. The microstructures, fracture surface and interface of the Cr$_3$C$_2$/Al$_2$O$_3$ were examined by scanning and transmission electron microscopes (SEM and TEM). The electrical resistivity was measured by the two-terminal method using a high-resistance meter. Gold was vapour-deposited by sputtering on both sides of the rectangular testing bars ($3 \times 4 \times 10$ mm) to form electrodes. The Al$_2$O$_3$ grain size was evaluated by the line-intercepted method after the samples had been etched in hot phosphoric acid.

3. Results and discussions
3.1. Densification and microstructures
Fig. 1 shows the relative density as a function of hot-pressing temperature for Al$_2$O$_3$-based composites containing ~10–40 vol % Cr$_3$C$_2$(M) particles. The densification of Al$_2$O$_3$–Cr$_3$C$_2$ composites is dependent on the hot-pressing temperature and Cr$_3$C$_2$ particle content. A tendency of inhibition of densification of the composite compacts by the Cr$_3$C$_2$ additions is clearly observable. Therefore a higher sintering temperature is needed to obtain a fully dense composite with higher Cr$_3$C$_2$ particle content. For example, $T \geq 1350$°C for 20 vol % Cr$_3$C$_2$, $T \geq 1450$°C for 30 vol % Cr$_3$C$_2$, and $T \geq 1550$°C for 40 vol % Cr$_3$C$_2$ composites are required to obtain a more than 99% relative density. A reduction in the rate of densification caused by the presence of these rigid inclusions or reinforced second phase is well documented in many theoretical and experimental studies [10–13].

According to their experimental results, the formation of a constrained network [10,11] and interactions [12] between rigid inclusions will give rise to differential shrinkage characteristics of the matrix and inclusions, and will cause sintering damage such as crack-like flaws or pores. The presence of a second-phase particle will raise the sintering activation energy [13] despite both constant heating rate and isothermal sintering processes. Thus a higher driving force, achieved by raising the temperature, is needed to overcome these obstacles to densification when the Cr$_3$C$_2$ content particle is high.

The SEM micrographs observed from the polished surface of dense 30 vol % Cr$_3$C$_2$(M)/Al$_2$O$_3$ composites sintered at 1400 and 1700°C are shown in Fig. 2a and b, respectively. The particle size of Cr$_3$C$_2$ for composites sintered at 1400°C is ~2 μm, as shown in Fig. 2a, very close to the size of the raw Cr$_3$C$_2$ particles. As the sintering temperature rises to 1700°C, the average particle of Cr$_3$C$_2$ is close to 8 μm. The growth of Cr$_3$C$_2$ particles is very rapid with the increase of temperature, indicating that Cr$_3$C$_2$ must possess sufficient self-diffusion. The main mechanism of Cr$_3$C$_2$ particle growth is coalescence. The formation of necks between Cr$_3$C$_2$ particles along Al$_2$O$_3$ grain boundaries can be seen in Fig. 3. The growth of Cr$_3$C$_2$ particles by coalescence proceeded in order to decrease the total surface energy. The morphology of Cr$_3$C$_2$ changes from a small spherical single crystal to a large irregular chain-like polycrystalline particle, as illustrated in Fig. 2. The Cr$_3$C$_2$ grain boundaries were easily observed after chemical etching, and the different orientation of individual Cr$_3$C$_2$ grains within a large irregular particle was also verified by TEM diffraction patterns. The rate of Cr$_3$C$_2$ coalescence is a function of sintering temperature and Cr$_3$C$_2$ content in the composites. Higher sintering temperature, resulting in a greater diffusivity, and high Cr$_3$C$_2$ content giving a shorter mean free path, produce a greater rate of coalescence of Cr$_3$C$_2$ particles. Thus for 40 vol % Cr$_3$C$_2$/Al$_2$O$_3$ composites, some coalescence is affected even when hot-pressed at 1400°C, because the mean free path is very short.

Fig. 4 indicates that the average grain size of Al$_2$O$_3$ is a function of Cr$_3$C$_2$ content in composites hot-pressed at various temperatures. There is no grain growth until relative density approaches ~90% [14,15] for a high-purity Al$_2$O$_3$ powder with a submicrometre diameter in the initial sintering stage.