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Densification and mechanical properties of WC particulate reinforced Cr_3C_2 matrix composites

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The mechanical properties of Cr_3C_2 can be improved by adding 14–25 vol % of WC particulates through a hot-pressing process. The Cr_3C_2–20 vol % WC composite exhibits a fracture strength and fracture toughness of 883 MPa and 6.8 MPa $m^{1/2}$, respectively, which is a better than 60% increase over the monolithic Cr_3C_2 (σ_f = 526 MPa, K_{IC} = 4.1MPa $m^{1/2}$). The possible strengthening and toughening mechanisms are disscussed in terms of microstructures, fracture modes (intergranular or transgranular) and micromechanics. The microstructural evolution and fractography which were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) will be discussed.

1. Introduction

Ceramic matrix composites have recently come to prominence for structural applications because of their attractive mechanical properties either at ambient or elevated temperatures.

Monolithic chromium carbide (Cr_3C_2), due to its excellent physical properities such as high melting temperature, strength, hardness as well as corrosion resistance, is one of the most popular carbides used in wear and steel-making industries [1, 2]. Unfortunately, its intrinsic brittleness makes its reliability low thus preventing wider usage. To reduce this serious drawback, various methods have been investigated to increase its toughness. Amongst them, using hard ceramic particles as a reinforcement phase has been demonstrated as being very effective in strengthening and toughening chromium carbide [3, 4].

In addition to a high modulus and electrical conductivity, tungsten carbide (WC) possess outstanding high-temperature erosion resistance. It thus might be a suitable candidate as a dispersed phase to reinforce Cr_3C_2. In this study, preliminary findings on WC reinforced Cr_3C_2 are reported. The correlations amongst the densification, microstructures and mechanical properties of Cr_3C_2 matrix composites with the incorporation of 14–25 vol % Cr_3C_2 particles are reported.

2. Experimental procedures

2.1. Raw materials

The Cr_3C_2 and WC powders H.C. Stark (Berlin, Germany) used in this investigation had a purity higher than 99%. The mean particle size measured by laser diffraction techniques is 1.5 μm and 1.6 μm for the Cr_3C_2 and WC, respectively.

2.2. Consolidation procedures

The Cr_3C_2 and WC powders were mixed together using deionized water and then ball-milled for 24 h. The dried and sieved mixture was uniaxially prepressed 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 at temperatures ranging from 1400–1700 °C in an Ar atmosphere, under a pressure of 30 MPa for 1 h.

2.3. Characterization

The dense composite discs were ground and cut along the grinding direction, to form 3 × 4 × 40 mm bars. All specimens were polished with diamond paste of grades between 15 μm and 3 μm. The flexural strength was measured through a 4-point bending test following the JIS 1610 method and the fracture toughness was evaluated using the single-edge-notched beam (SENB) method. Both of these properties were measured at room temperature. Each bar used in the fracture toughness test, was centre-notched to one-third of its thickness using a 0.15 mm-thick diamond blade. The microstructures, fracture surfaces and interfaces of the WC/Cr_3C_2 composites were examined by using a scanning electron microscope (SEM) and a transmission electron microscope (TEM), with the grain size being evaluated by the line intercept method.

3. Results and discussion

3.1. Densification and microstructures

Fig. 1 shows the relative density as a function of hot-pressing temperature for Cr_3C_2 based-composites containing 0–25 vol % WC particles. The densification of the Cr_3C_2–WC composites is dependent on the hot-pressing temperature and WC content. The hindrance to the densification of the composite produced

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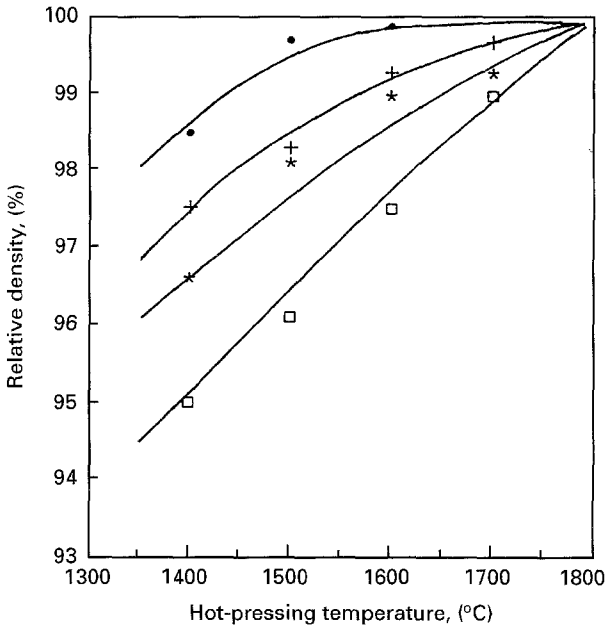

Figure 1 The relative density as a function of hot-pressing temperature and WC content for Cr_3C_2–WC composites. The contents are; (●) pure Cr_3C_2, (+) 14 vol % WC, (*) 20 vol % WC and (□) 25 vol % WC.

by the WC particles is clearly observable. Therefore, at high WC contents a higher sintering temperature is required in order to obtain fully dense composites. For example, a temperature of 1600 °C is required at a 14 vol % WC concentration and a temperature of 1700 °C is required at a 20 vol % WC concentration if the WC/Cr_3C_2 composites are to become more than 99% dense. The phenomenon of a reduction in the densification rate caused by the presence of rigid inclusions is documented in many theoretical and experimental studies [5, 6]. The formation of a constrained network [5] and interactions between rigid inclusions [6] give rise to differential shrinkage characteristics between the matrix and the inclusions which can result in the formation of cracklike flaws and pores. Thus a higher driving force, achieved by means of raising the temperature, is needed to overcome these obstacles in order to densify the WC/Cr_3C_2 composites at high WC contents.

A TEM micrograph of a dense 14 vol % WC/Cr_3C_2 composite sintered at 1600 °C is shown in Fig. 2a. The particle size of WC in the composite sintered at 1600 °C is about 1.2 μm which is very close to the particle size of the WC powder. The WC particles located at grain boundaries or the triple junctions of Cr_3C_2 grains are effective in inhibiting the grain growth. In Fig. 3, it is shown that the average grain size of Cr_3C_2 in composites hot-pressed at 1500 °C and 1600 °C is much hindered by WC content. For instance the Cr_3C_2 grain size is reduced form 8.8 μm for monolithic Cr_3C_2 to 6.1 and 4.6 μm for 14 and 25 vol% WC contents, respectively, when the hot-pressing temperature is 1600 °C. The unchanged WC particle size indicates a low self-diffusivity and gives a low migration rate. When it is not entrapped into the grains, it produces a strong dragging force [8] that retards the migration of Cr_3C_2 grain boundaries.

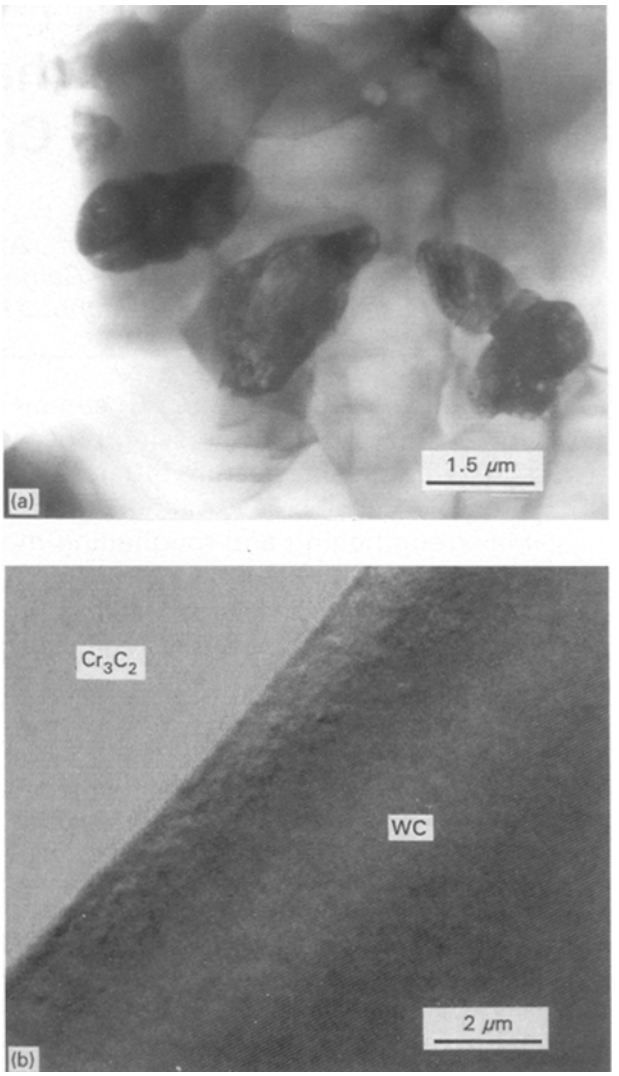

Figure 2 TEM micrographs of Cr_3C_2–14 vol % WC composites hot-pressed at 1600 °C. (a) The WC particles (black) are located at the grain boundaries of the Cr_3C_2 matrix (white). (b) The interface between Cr_3C_2(white) and WC (black).

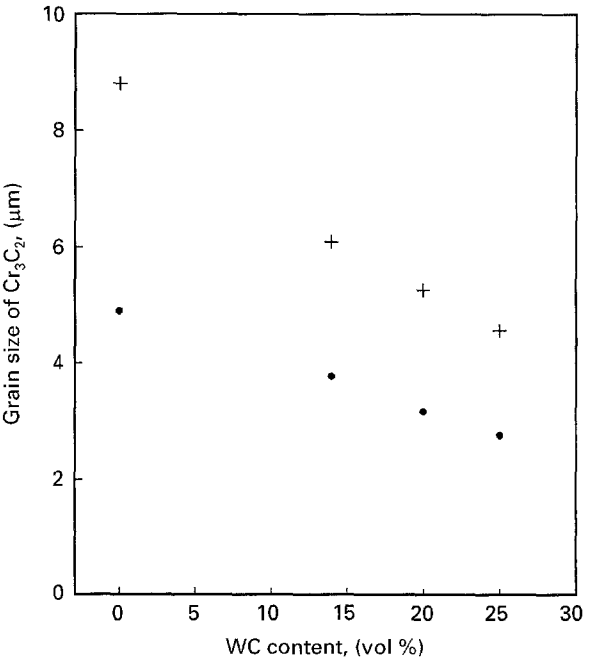

Figure 3 The average Cr_3C_2 grain size dependency on WC content for Cr_3C_2–WC composites hot-pressed at; (●) 1500 °C and (+) 1600 °C.

Therefore, refined grain size in addition to uniformly distributed small WC particles produce a strong and tough WC/Cr_3C_2 composite as will be discussed in the next section.

A relatively weaker interface [7] is important in toughening non-transformation ceramic composites. The selected reinforcements must not chemically react with the matrix phase. In the Cr_3C_2–WC composite system, X-ray diffraction analysis of hot-pressed composites indicated that there is no chemical reaction between Cr_3C_2 and WC. A HRTEM micrograph of the interface between WC and Cr_3C_2 is shown in Fig. 2b, and no evidence of a reaction layer existing in the interface was observed. Thus, Cr_3C_2 and WC are chemically inert to each other and do not react during the hot-pressing process.

3.2. Mechanical properties

The fracture strength of the densified composites as a function of WC content is shown in Fig. 4. The fracture strength of all Cr_3C_2–WC composites hot-pressed above 1400 °C are always higher than that of monolithic Cr_3C_2 (~ 526 MPa). These results indicate that the incorporation of WC particles into the Cr_3C_2 matrix can significantly enhance the strength of pure Cr_3C_2. The trends of variation in the fracture strength with the hot-pressing temperature for Cr_3C_2–WC composites incorporating three different WC contents are similar. For Cr_3C_2–20 vol % WC hot-pressed composites, the fracture strength is improved from 617 MPa at 1400 °C to 883 MPa at 1600 °C which is produced by the higher density. Then, the fracture strength is slightly reduced to 776 MPa at 1700 °C which resulted from the larger Cr_3C_2 grain size.

The fracture surfaces of Cr_3C_2 and Cr_3C_2–20 vol % WC composites hot-pressed at 1600 °C are illustrated in Fig. 5(a, b), respectively. The fracture mode is evidently changed from a dominant intergranular mode for monolithic Cr_3C_2 (see Fig. 5a) to an almost completely transgranular mode for WC/Cr_3C_2 composites (see Fig. 5b). The fracture strength associated with the transgranular fracture mode is always greater than that of the intergranular fracture mode for the monolithic ceramic [9] or ceramic matrix composites [10]. Another important factor has to be considered, namely the residual stress, which is generated from the large thermal expansion mismatch. The thermal expansion coefficient (TEC) of Cr_3C_2 ($11.2 \times 10^{-6}\,°C^{-1}$) is greater than the TEC of WC ($6.89 \times 10^{-6}\,°C^{-1}$). The magnitude and direction of the thermal residual stress which developed at the interfaces during cooling down from the fabrication temperature were evaluated [11]. A compressive residual stress of about 2 GPa acts on the Cr_3C_2 matrix in the radial direction. The transgranular fracture mode coupled with the compressive stress in the Cr_3C_2 matrix and the much refined grain size, give a higher fracture strength for WC particle reinforced Cr_3C_2 composite than that of monolithic Cr_3C_2.

The fracture toughness values for the composites as a function of WC content are presented in Fig. 6. The fracture toughness of Cr_3C_2–WC composites initially increases with densification and gives a peak

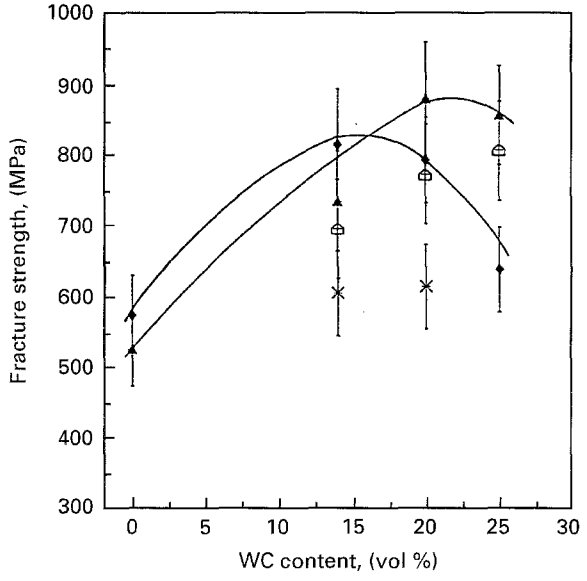

Figure 4 Fracture strength of Cr_3C_2–WC composites as a function of WC content. The hot pressing temperatures investigated were; (×) 1400 °C, (◆) 1500 °C, (▲) 1600 °C and (⏢)1700 °C.

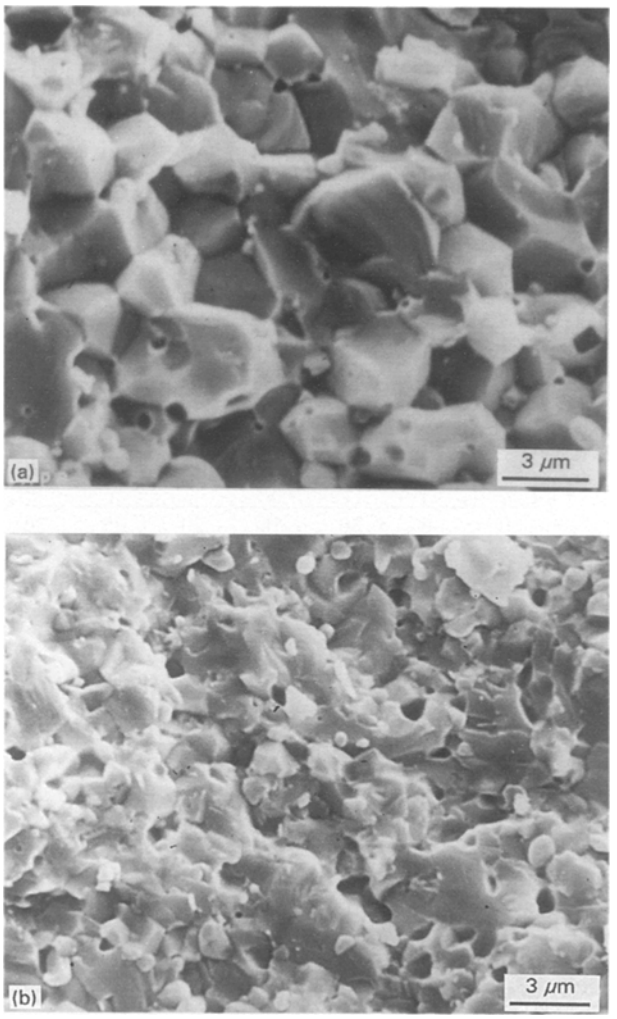

Figure 5 Fracture surface of (a) pure Cr_3C_2 and (b) Cr_3C_2–20 vol% WC composites hot-pressed at 1600 °C. They exhibit dominant intergranular and transgranular fracture, respectively.

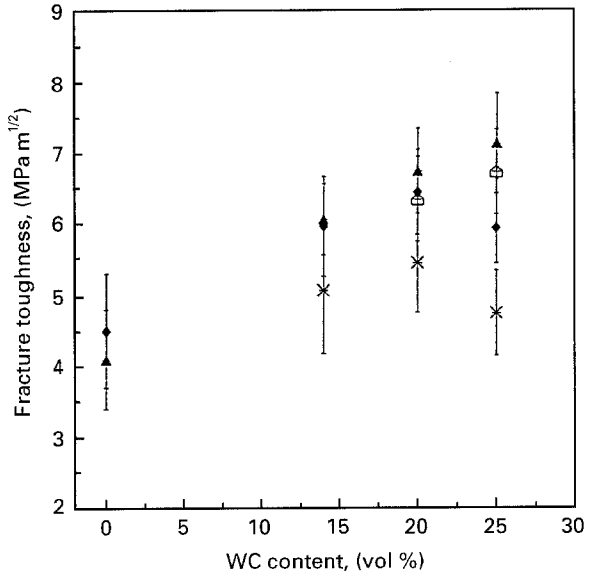

Figure 6 Fracture toughness of Cr_3C_2–WC composites as functions of WC content. The hot-pressing temperatures investigated were (×) 1400 °C, (◆) 1500 °C, (▲) 1600 °C and (⏢) 700 °C.

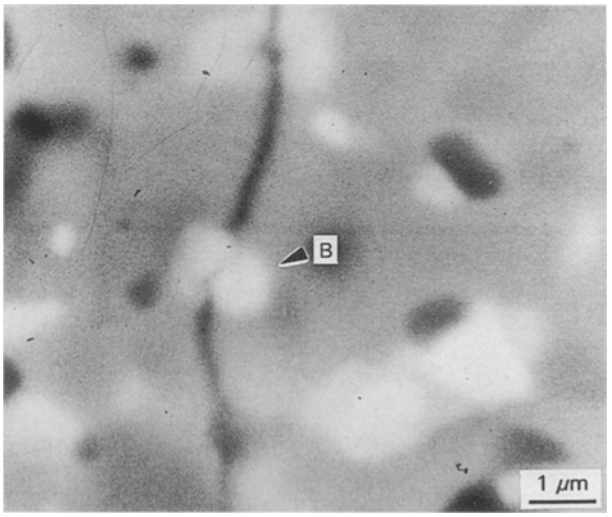

Figure 7 SEM micrograph of the interaction between a microcrack induced by the Vickers indentor and a WC particle in Cr_3C_2–20 vol % WC composites. A crack bridging effect is observed (as indicated by the B arrow).

value of 6.1, 6.8 and 7.2 MPa m$^{1/2}$ at 14, 20 and 25 vol % WC content, respectively. The interactions between Cr_3C_2 particles and the crack induced by the Vickers indentor are revealed in Fig. 7. It is apparent that the primary toughening mechanism is crack bridging. According to a mechanical analysis of the bridging model for particle [7] or whisker [12] reinforced ceramic matrix composites, the toughening effect is proportional to the content of the reinforcing phase. A high content of reinforcing particulates can provide good toughening characteristics.

Based on the stored elastic strain energy converting to the work of fracture in the composite materials, Rice [12] and Tsukuma *et al.* [13] proposed that there is a critical particle size (*Ds*) for the second phase beyond which a spontaneous microcracking would occur. The critical spherical particle size is determined

TABLE I The approximate parameters and resultant estimates for *Ds* in Cr_3C_2–WC composites determined by Equation (1)

Composite	$\Delta\alpha$ ($\times 10^{-6}\,°C^{-1}$)	ΔT (°C)	E (GPa)	γ (Jm^{-2})	Ds (μm)
Cr_3C_2–WC	4.31	1200	385	1	0.94

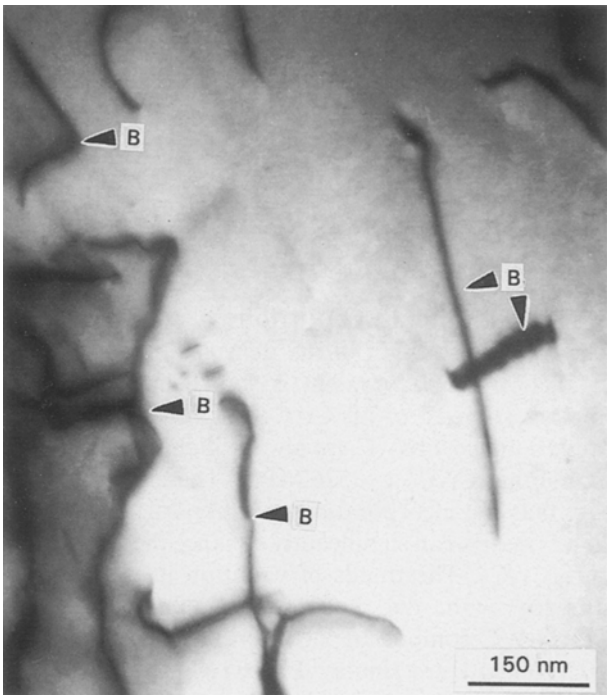

Figure 8 TEM micrograph showing the dislocation lines (as indicated by the B arrows) within the WC particles.

by several factors as indicated by Equation (1).

$$Ds \fallingdotseq -\frac{10\,\gamma_m}{(\Delta\varepsilon)^2 E} \quad (1)$$

where γ_m is the fracture energy for microcracking, $\Delta\varepsilon$ is the particle–matrix mismatch strain ($\sim \Delta\alpha\Delta T$ where $\Delta\alpha$ is the thermal expansion mismatch and ΔT = the temperature difference over which the elastic strain builds up) and E is the Young's modulus of the matrix material.

Approximate parameters and the resultant estimates for *Ds* in Cr_3C_2–WC composites are shown in Table I. The critical WC particle size in Cr_3C_2–WC composites is about 0.94 μm. Although the average particle size of the WC particles dispersed in the composites exceeds this critical size, no microcracking is observed in the Cr_3C_2/WC interfaces (see Fig. 2b). However, it is interesting to note that dislocation lines within the WC particles are clearly observable as indicated in Fig. 8. Since no dislocation lines are found within the raw WC powders, it is reasonable to suggest that the dislocation lines arise from the plastic deformation which is created from the residual thermal stress exceeding the yield stress in the WC crystals. Owing to the presence of dislocations, both the practical residual thermal stress and elastic strain energy at the Cr_3C_2/WC interfaces significantly decrease. Nevertheless, the thermal mismatch leaves

a residual stress which will attract perpendicularly propagating cracks toward the WC particles. A crack pinning effect might be playing a minor role on toughening these composites.

4. Conclusion

The Cr_3C_2–WC composite can be densified by hot-pressing at 1600 °C to greater than 98.5% relative density. The addition of WC particles to the Cr_3C_2 matrix can retard the densification and inhibit the grain growth of the Cr_3C_2 matrix. Experimental data show that the incorporation of WC particles can effectively strengthen and toughen the Cr_3C_2 ceramics. A transgranular fracture mode and a residual compressive stress in the matrix phase are the primary strengthening mechanisms. The toughening effect is mainly due to a crack bridging machanism with a possible extra minor contribution coming from crack pinning by WC particles.

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