Thermal conduction in Cr_3C_2/SiC composite

DEAN-MO LIU, BOR-WEN LIN
Materials Research Laboratories, Industrial Technology Research Institute, Hsingchu, Chutung, 31015, Taiwan, ROC

Thermal conduction behaviour of Cr_3C_2/SiC composite is investigated in terms of temperature and SiC content. Experimental results showed that thermal diffusivity of the composite increases with SiC content up to 20 vol%, corresponding to a conductivity maximum, then decreases with further increase of SiC. The reduction in diffusivity and conductivity at higher SiC content may due to formation of small amounts of solid solution at the interface and/or of interfacial gaps due to lack of perfect contact among SiC aggregates leading to increased phonon scattering. The thermal conductivity demonstrates a positive temperature dependence but becomes temperature-independent when SiC content is above 30 vol%. A correlation with composite theory is present.

1. Introduction

Chromium carbide (Cr_3C_2) has been widely used as precipitate-strengthening material in the steel and non-ferrous alloy industries for many years [1]. Its possession of sufficient strength as well as hardness with the inertness to metal/alloy at elevated temperatures make the material an interesting candidate in many metal industries. For instance, its high temperature stability, good oxidation and scale resistance allow Cr_3C_2 to be applied to a multi-type slab reheating furnace in the steel making industry [2]. In addition, chromium carbide has a low electrical resistance which allows electrical discharge machining for components having complex geometry [3].

In a previous study [4], the present authors have developed a composite material in a Cr_3C_2/SiC system by means of a hot-pressing technique. Due to large differences in coefficients of thermal expansion, i.e., $Cr_3C_2 \sim 11.4 \times 10^{-6}$/°C and SiC $\sim 4.2 \times 10^{-6}$/°C, a large residual compressive stress building up at the interface when cooling from processing temperatures is expected. This composite thus exhibited mechanical properties, such as bending strength and fracture toughness, superior to both its end compositions and comparable to those of silicon nitride. In addition, this composite has been found to demonstrate a superplasticity at elevated temperatures depending on SiC content, up to around 1200 °C at 30 vol% of SiC [4].

For structural applications as well as for considerations of increased thermal efficiency, a knowledge of the thermal conduction behaviour of the composite is essential, especially for design purposes. The thermal diffusivity and conductivity data of SiC are well-documented; unfortunately, limited data are available for chromium carbide [5, 6]. Therefore, besides a study on the thermal conduction in single-phase Cr_3C_2, this paper aims at investigating the

effect of SiC content and temperature on thermal transport properties of the Cr_3C_2/SiC composite. Effect of microstructure orientation upon hot-pressing direction on thermal diffusivity is described and a correlation with composite theory is presented.

2. Experimental procedures

Fine-grained chromium carbide (1.5 μm, Hermann C. Starck) and SiC powders (0.5 μm, Showa Denko A-1) with 0–40% volume were mixed by ball-milling for 20 h with ethanol solution as medium. The mixed powder was oven-dried at 150 °C, shaped to form a cake 6 cm in diameter and 1 cm in thickness, then hot-pressed under a uniaxial pressure of 30 MPa in an induction-heating furnace to 1300–1450 °C for 4 h in vacuum (6.5×10^{-2} Pa). The resulting composites, having densities of above 98.5% of theoretical determined by Archimede's method, were polished and punched ultrasonically into a disc with dimensions of approximately 10 mm in diameter and 1.3 mm in thickness and used for thermal diffusivity and conductivity measurements. Densities of the composites were measured by a water displacement technique. A scanning electron microscope (SEM, Cambridge Instruments, S-360) was used for microstructure examination.

A laser-flash instrument (ULVAC, SINKU-RIKO Inc., Model TC-3000H) was employed to measure the thermal diffusivity (α) and specific heat (C_p) of the specimens simultaneously [7] from room temperature to 600 °C. A ruby laser is used as an energy source which has a beam size of 10 mm diameter; the infrared detector is liquid-nitrogen-cooled InSb. For thermal diffusivity measurement, the specimen surfaces were coated with colloidal graphite to promote the absorption of incident energy pulses during the test. The sample was held in vacuum in an electric furnace

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for high temperature measurement. The thermal diffusivity (α) is thus obtained as follows

$$\alpha = 1.38L^2/\pi^2\tau \qquad (1)$$

where L is the sample thickness and τ is the time taken for the temperature of the sample rear surface to reach half of the maximum value after the sample front surface has been irradiated by an instant heat source. Five shots were made for each measurement.

For specific heat (C_p), the specimens were prepared in a similar fashion to that for measurements of thermal diffusivity; an additional Pt–Rh thermocouple wire with diameter 0.1 mm was attached by a silver paste to the rear surface of the specimen followed by 4-h curing at 150 °C. The C_p is then given by

$$C_p = Q/\rho w \Delta T_{max} \qquad (2)$$

where w is the sample weight and ΔT_{max} is the maximum temperature increase of the sample when irradiated with the energy pulse. Thus, the thermal conductivity (K) was determined by;

$$K = C_p \alpha \rho \qquad (3)$$

where ρ represents the bulk density of the composite and the measurement error is within 5% verified by a sapphire standard.

3. Results and discussion

Fig. 1 shows the values of thermal diffusivity of the composite in terms of temperature with varying SiC contents. For monolithic Cr_3C_2 ceramic, the thermal diffusivity showed a negative dependence below 300 °C and became positively temperature-dependent of diffusivity up to 600 °C. Since Cr_3C_2 has a low electrical resistivity, i.e., $68\,\mu\Omega\,cm^{-1}$, over which few electrons may be free to move in a certain way in Cr_3C_2; thereby, the thermal transport in Cr_3C_2 may be contributed to by a combination effect of both phonon and electron. At lower temperatures where phonon conduction is predominant and leads to a

typical negative temperature dependence of thermal diffusivity, while electrons might play an important part at higher temperatures.

Similar trends are observed for the composite with SiC content up to 20 vol %, nevertheless, higher temperature dependence was observed with increasing SiC content indicating the increased phonon–phonon contribution due to SiC. It is interesting to note that the diffusivity decreased again for temperatures above 450 °C; the reasons are unclear, but may probably result from the effect of SiC on reduction of heat conduction rate due to increased phonon scattering at elevated temperatures [8]. A negative temperature dependence was observed over the temperature range for higher SiC content, i.e., 30 vol %. The nearly T^{-1} dependence indicating that the thermal conduction is essentially controlled by phonon–phonon scattering as shown by Peierls [8], who indicated that the phonon mean free path due to scattering by anharmonic vibration of lattice to be proportional to the inverse of absolute temperature, and which may further substantiate the increased phonon scattering effect mentioned earlier.

Considering the effect of SiC on thermal diffusivity depicted in Fig. 2, at both ambient and elevated temperatures, the diffusivity increased with SiC up to 20 vol %. This is expected in general from composite theory, which shows that a dispersed phase with high thermal conductivity within a matrix with low thermal conductivity results in an increase in overall thermal conductivity, and vice versa, a decrease in overall conductivity, regardless of the size and distribution of the dispersed phase [9–11]. However, further increase of SiC content decreases the diffusivity, which seems to contradict the expectation of composite theory. A general explanation for most of composites is the formation of an interfacial gap between the dispersed and matrix phase due to the difference in thermal expansion coefficient [12,13]. However, it is impractical for the present composite material because the matrix has a higher thermal expansion coefficient than
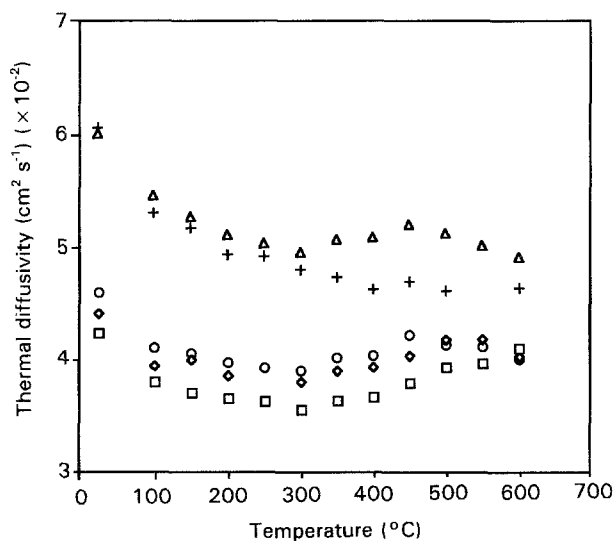

Figure 1 Temperature dependence of thermal diffusivity for Cr_3C_2/SiC composite. □, 0%; ◇, 5%; ○, 10%; △, 20%; +, 30%.

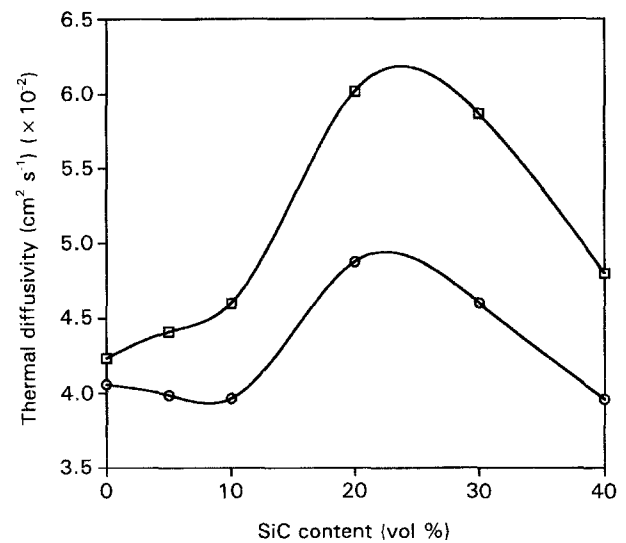*Figure 2* Thermal diffusivity of Cr_3C_2 composite in terms of various SiC contents at 25 °C (○) and 600 °C (□).

the dispersed SiC particle and the dispersant surface should be exerted by a residual compressive stress as high as 250 000–300 000 p.s.i. when the composite is cooling from about 1000 °C [4], where no stress relaxation has been assumed to take place, according to [14]

$$S_f = \frac{\Delta\alpha\Delta T E_d}{(1 + v_m)(E_d/2E_m) + (1 - 2v_d)} \qquad (4)$$

where $\Delta\alpha$ is the difference of thermal expansion coefficient, E and v are modulus and Poisson's ratio of the material respectively, the subscripts d and m represent the dispersed and matrix phase respectively. Therefore, a perfect contact between the SiC particle and Cr_3C_2 phase is expected.

At higher SiC concentration especially for 40 vol % SiC, the SiC phase is nearly continuous; another explanation based on agglomeration of SiC particles is thus proposed. To obtain a dense body, a higher firing temperature, i.e. 1450 °C, was employed for the composites with 30 vol % and 40 vol % SiC. However, the temperature is too low for SiC agglomerates to have a completely sintering behaviour, i.e. SiC particles are in contact physically without the formation of a well-developed grain boundary. Hence, considerable amounts of interfacial gap may be present between contacting SiC particles due to particle geometry factors and/or surface roughness of the particle, and is assumed to distribute randomly through the composite. These interfacial gaps may have widths of tenths of microns and are expected to act as a barrier to heat flow (referred to as a contact resistance [15]), which in turn, increases phonon as well as electron scattering, and consequently, decreases thermal diffusivity. If this is true, the higher values of thermal diffusivity for 30 vol % and 40 vol % SiC-contained composite than that for single-phase Cr_3C_2 indicates the contribution of SiC to thermal conduction.

Nevertheless, if the interfacial gap does exist among SiC particles, it may weaken the strength [4], the maximum strength appears at the composite with 30 vol % SiC but decreases significantly at 40 vol % of SiC content. Since the SiC phase is more possibly a continuous phase for the latter composition than for the former one, therefore this does not seem likely to be the only reason. A more plausible explanation is a combination effect of the interfacial gaps together with the formation of small amounts of solid solution at the interface between SiC and Cr_3C_2 due to higher processing temperatures, although no conclusive evidence for such an assumption is substantiated. The solid solution is known to have a significant effect on reducing the phonon mean free path [16, 17] and is assumed to play a major role in phonon scattering for composite with 30 vol % SiC, whereas both effects are assumed to be important for the 40 vol % SiC-contained composite.

The roughly parallel behaviour of thermal diffusivity with respect to SiC concentration at various temperatures in Fig. 2 indicates that the interfacial barrier together with solid–solution scattering are independent of temperature. The electronic contribution

TABLE I Values of specific heat ($J g^{-1} K$) and density ($g cm^{-3}$, in parentheses) of the Cr_3C_2/SiC composite in terms of various SiC contents and temperatures

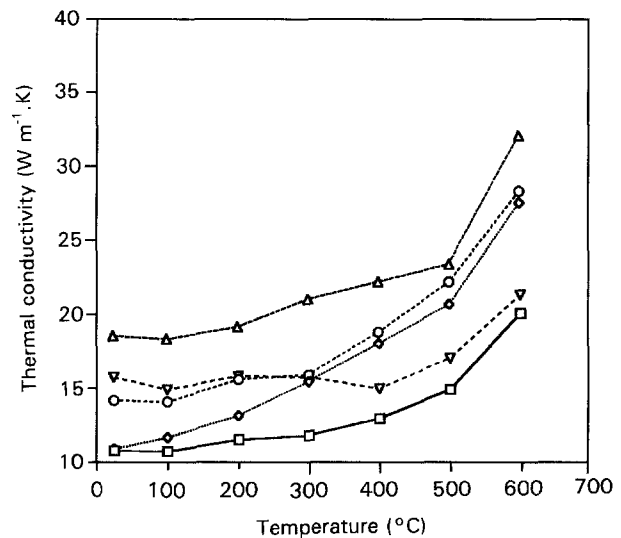| SiC	0%	5%	10%	20%	30%	40%
	(6.524)	(6.43)	(6.30)	(5.96)	(5.56)	(5.26)
25 °C	0.40	0.465	0.489	0.517	0.505	0.416
100 °C	0.431	0.537	0.542	0.561	0.545	0.51
200 °C	0.479	0.618	0.619	0.625	0.62	0.556
300 °C	0.502	0.732	0.642	0.706	0.632	0.67
400 °C	0.534	0.736	0.732	0.725	0.622	0.69
500 °C	0.572	0.794	0.767	0.758	0.708	0.703
600 °C	0.766	1.09	1.085	1.088	0.885	0.859

Figure 3 Temperature dependence of thermal conductivity for Cr_3C_2 composite. □, 0%; ◇, 5%; ○, 10%; △, 20%; ▽, 30%.

to heat conduction of Cr_3C_2 appears to play a minor role in the composite with higher SiC concentration at elevated temperatures [18], since electron scattering due to imperfect contact together with the electrical insulation effect of the SiC particles must also be taken into consideration [19].

Table I gives the specific heat of the composite at different temperatures. The specific heat increases with temperature and with SiC content up to 20 vol %, but decreases slightly with a further increase of SiC content. By multiplying the values of thermal diffusivity, specific heat, and density according to Equation 3, the values of thermal conductivity of the composite are determined with the consideration of dimensional change during heating, as illustrated in Fig. 3. The thermal conductivity of the composite showed a positive temperature dependence with SiC content below 30 vol %, while above 30 vol % the conductivity appears to be independent of temperature over 500 °C. This is essential for design purposes, because for a constant thermal conductivity, a linear temperature gradient and negligible thermal stress result while subjected to a linear heat flow.

Fig. 4 shows the effect of hot-pressing direction on the thermal diffusivity of the composite with 30 vol % SiC content. The specimens used for the measurement were prepared by cutting from one composite sample in different directions. It is clear to see that the
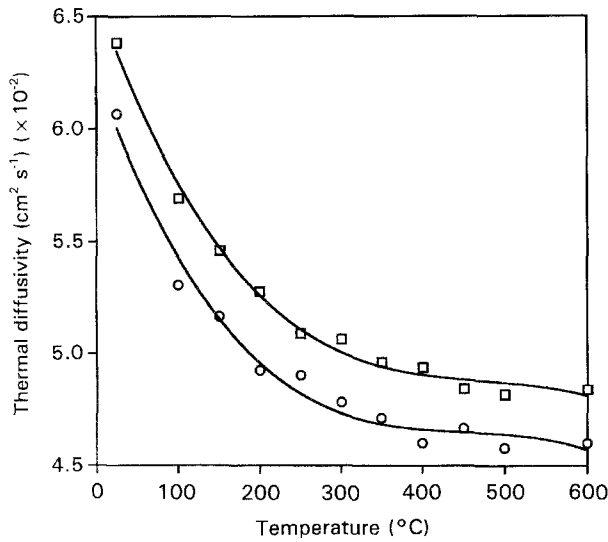
Figure 4 Thermal diffusivity of the composite with 30 vol % SiC as a function of temperature and hot-pressing direction. □, parallel, ○, perpendicular.
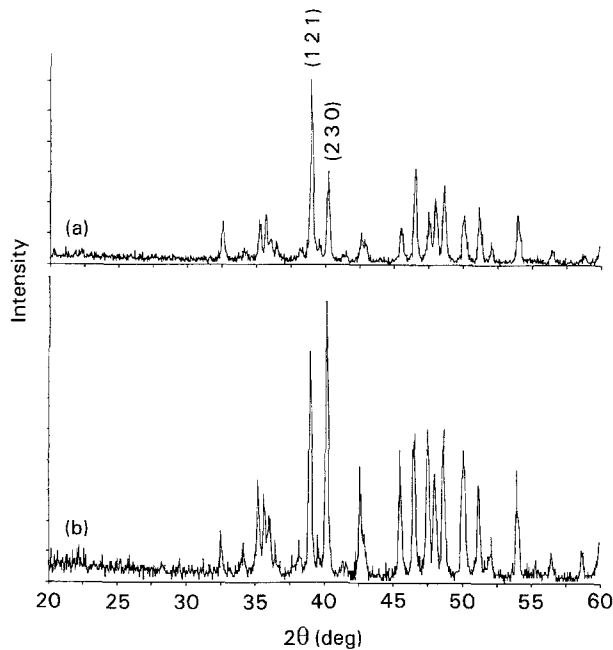

Figure 5 X-ray diffraction patterns of the composite with 30% SiC with direction (a) parallel and (b) perpendicular to the hot-pressing direction.

specimen with direction parallel to the hot-pressing direction has values of thermal diffusivity higher by about 10% than those perpendicular to the hot-pressing direction. This finding suggests a microstructure effect as those observed in other composite systems especially for composites with short fibres or whiskers as a dispersed phase [20, 21]. For the present composite in which particulate SiC is the only secondary phase, the resulting anisotropic thermal conduction property may thereby arise from Cr_3C_2 grains. Unfortunately, no considerable difference in respective microstructure can be differentiated by SEM examination [4]. As a continuous phase, the Cr_3C_2 grains may grow in a preferred orientation according to the hot-pressing direction. This was evidenced by X-ray diffraction patterns in Fig. 5, where crystallo-

graphic (1 2 1) plane is preferred in a parallel direction while the (2 3 0) plane is preferred in a perpendicular direction. This indication suggests that by adjusting the crystallographic orientation of Cr_3C_2 crystals upon manufacturing, composites with controllable thermal transport properties can be achieved to meet various requirements.

Hasselman et al. [13] derived a series of expressions by modifying the original composite theories of Rayleigh [10] and Maxwell [11] by considering the effect of interfacial thermal resistance. These expressions allow the prediction for the effective thermal conductivity of composite consisting of a homogeneous matrix phase in which particles of a second homogeneous phase are dispersed. For spherical dispersions the equation is given by

$$K_{eff} = K_m \left[2\left(\frac{K_d}{K_m} - \frac{K_d}{ah} - 1\right)V_d \right.$$

$$+ \frac{K_d}{K_m} + \frac{2Kd}{ah} + 2 \right] / \left[\left(1 - \frac{K_d}{K_m} + \frac{K_d}{ah}\right)V_d$$

$$+ \frac{K_d}{K_m} + \frac{2K_d}{ah} + 2 \right]^{-1} \quad (5)$$

where K_{eff} is the effective thermal conductivity of composite, a is the radius of a sphere, h is the interfacial thermal conduction coefficient, and V is the volume fraction of the dispersion. In the absence of interfacial thermal resistance, i.e., $1/h = 0$, Equation 5 agrees with Maxwell's theory for K_{eff} and is also consistent with Eucken's relation [22] for the case of a continuous phase with spherical inclusion. By employing Equation 5, with $1/h = 0$, to the present composite (Fig. 6), the predicted values of thermal conductivity (solid line) are in general agreement with the experimental measurements (room temperature data) up to 20 vol % of content. The results also confirm the perfect contact between SiC and Cr_3C_2 previously mentioned. Large deviations occur for higher SiC
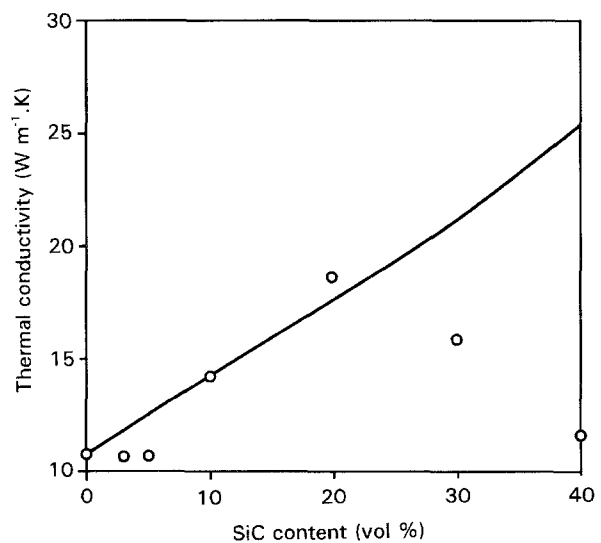

Figure 6 Thermal conductivity of the Cr_3C_2/SiC composite as a function of SiC content in comparison with theoretical prediction. Straight line, Equation 5 with $1/h = 0$.

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contents, i.e., for the cases of 30 vol % and 40 vol %, indicating the presence of other factors such as interfacial gaps in SiC aggregates and a solid–solution effect affecting the heat conduction mode.

4. Conclusion

Thermal conduction properties of Cr_3C_2/SiC composite have been investigated. For monolithic Cr_3C_2, heat transport is primarily controlled by phonon and electron; phonon conduction characteristics become more pronounced with further increase of SiC. A maximum value of thermal diffusivity as well as conductivity can be reached at 20 vol % SiC content. However, the conductivity decreases significantly for 30 and 40 vol % content which may be postulated as a combination effect of an interfacial gap that forms between poorly-sintered SiC particles and formation of small amounts of solid solution between SiC and Cr_3C_2. The composite with 30 vol % SiC content demonstrates a lower and temperature-independent thermal conductivity, and this together with the superior mechanical properties demonstrated by our previous investigation, suggests it to be a prime candidate for improving energy efficiency in energy-conversion systems.

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