

Thermal Properties of Ti-SiC- and Ti-TiB₂-Reinforced Composites¹

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Thermal conductivity data are presented for titanium-based composites reinforced with 10 and 20%, by volume, of SiC and TiB₂ particles and for a composite reinforced by 10%, by volume, of SiC short fibers. In each case the thermal conductivity of titanium would be expected to be enhanced by the presence of the reinforcement. Measurements were made on the composites both as fabricated and after heat treatment. The results clearly show that the thermal conductivity of the Ti-SiC is much lower than predicted and decreases still further after heat treatment. This is attributed to the production of an interfacial contact resistance as a result of crack generation in the reaction products. A smaller effect is noted in the Ti-TiB₂ composites.

KEY WORDS: metal matrix composites; thermal conductivity; titanium composites.

1. INTRODUCTION

It is being increasingly recognized that transport properties such as thermal and electrical conductivity may be of considerable significance for advanced composites in various potential applications. Thermal conduction also plays an important role in thermal shock behavior. For most metal composites the reinforcement generally has a lower thermal conductivity than the matrix. However, SiC and TiB₂ both have a higher thermal conductivity than titanium. Hence, an enhancement of thermal conductivity is expected to occur from the presence of both types of reinforcement.

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Enhancement (or even retention) of the matrix thermal conductivity in a composite requires the transport of heat across the matrix–reinforcement interface. There is very little published information about how efficiently this can occur in metal–matrix composites.

Titanium-based composites are particularly prone to interfacial chemical reaction during processing and in high-temperature service. Such reactions can impair mechanical properties and will affect the thermal conductivity.

In this paper, experimental data are presented for Ti–SiC and Ti–TiB₂ particulate composites, with and without substantial heat treatments, and for a short-fiber composite of Ti–SiC. The composites were produced by powder blending and extrusion. Thermal diffusivities of these composites were measured as a function of temperature using the laser flash technique. Thermal conductivities were derived from these data using a rule of mixtures assumption for reference book specific heat data and measured densities.

2. EXPERIMENTS

2.1. Composite Production

Composites containing 10 and 20%, by volume, of reinforcement were made by dry blending of Ti powder (99.8% purity, 50- to 150- μm particle size) and either SiC or TiB₂ particulate (10- 30- μm diameter in both cases). The powder mixture was cold-pressed in a copper can, which was evacuated, heated, and sealed by electron beam welding prior to extrusion. The can was soaked for 2 h in a furnace at 900°C and then extruded in a circular section die of diameter 20 mm, with a die semi-angle of 45° and an extrusion ratio of about 17. A Ti–10 (vol%) SiC short-fiber composite was also made using Sigma SiC monofilament (W-cored, 100- μm diameter, chopped to \sim 5-mm lengths). The resulting material after extrusion was homogeneous and contained well-aligned SiC fiber with an average aspect ratio of about 3. An unreinforced Ti matrix extrudate was produced in exactly the same way as the composite.

2.2. Thermal Diffusivity Measurements

Thermal diffusivity measurements were made using the laser flash technique. The technique uses a small disk-shaped specimen, the front face of which is subjected to an instantaneous, uniform energy pulse. From the recorded temperature history of the opposite face the thermal diffusivity may be calculated [1].

In the UMIST apparatus [2] the heat pulse is supplied by a 100-J Nd/glass laser with a wavelength of $1.067 \mu\text{m}$, and the pulse dissipation time is 0.6 ms. The specimen, in a pyrolytic graphite sample holder, is heated to the measurement temperature inside a graphite susceptor located inside an induction coil. This assembly is located within a vessel that can operate either under vacuum ($< 10^{-5}$ Torr) or inert gas. Radiation from the specimen rear face is collected by a calcium fluoride lens and mirror system and focused onto an InSb infrared detector. The biased output from this detector is amplified and fed into microcomputer via an analog-to-digital convertor. The computer is programmed to calculate the thermal diffusivity, α , using the following equation:

$$\alpha = \frac{\omega/\pi^2 L^2}{t_{1/2}} \quad (1)$$

where ω/π^2 is a dimensionless heat term, L is the sample length, and $t_{1/2}$ is the time period required for the rear face of the specimen to reach half the maximum temperature rise. The boundary conditions for the flash method assume a homogeneous sample uniformly irradiated, negligible pulse duration time, and no heat losses. Corrections for finite pulse time are made using the method due to Clark and Taylor [3] and the term ω/π^2 is corrected for heat losses using the analysis due to Cowan [4]. Corrections for sample length change during heating were made using the thermal expansion coefficient of pure titanium [5]. The thermal conductivity, K , is the product of thermal diffusivity, α , density, ρ , and specific heat, C_p

$$K = \alpha \rho C_p \quad (2)$$

The composite densities were measured using the Archimedean displacement method and their specific heats calculated from the standard data values for titanium, SiC, and TiB_2 [5]. The specific heat values were fitted to a third-order polynomial over the measurement temperature range. The specific heat values of the composites were taken as a weighted mean between the values of the constituents. This apparently rather crude approach should be acceptable in view of the insensitivity of volume specific heat values to microstructural features, although it must be noted that the heavily reacted composites contained significant amounts of other phases.

Specimens were in the form of circular disks, 3 mm thick and 8 mm in diameter. These were machined from both composite and unreinforced extrudates so that the axis of the disk was parallel to the extrusion axis. In addition, specimens of SiC and TiB_2 were manufactured for thermal measurement, using the same ceramic powders as those employed for the

composites. The SiC specimens were produced by pressureless sintering at 2150°C, while for TiB₂ hot isostatic pressing was employed, at 1900°C and 50 bar. While the SiC was about 99% dense, the measured porosity level in the TiB₂ was about 27%; account was taken of these porosity levels in evaluating the true thermal conductivity of the two ceramics. Measurements were made during heating and cooling between 100 and 700°C. The two types of composite were heat treated by annealing for times up to 21 h at 950°C.

3. RESULTS AND DISCUSSION

3.1. As-Fabricated Specimens

It can be seen from Fig. 1. that while an enhancement of the thermal diffusivity/conductivity was expected from the presence of both particulate reinforcements, Fig. 2 shows that this behavior is observed only with the Ti-TiB₂ composites. The thermal conductivity of extruded Ti-TiB₂ composites is significantly greater than that of the unreinforced matrix and is enhanced with increasing volume fractions of reinforcement. In contrast, the thermal conductivity of the Ti-SiC composites is considerably lower

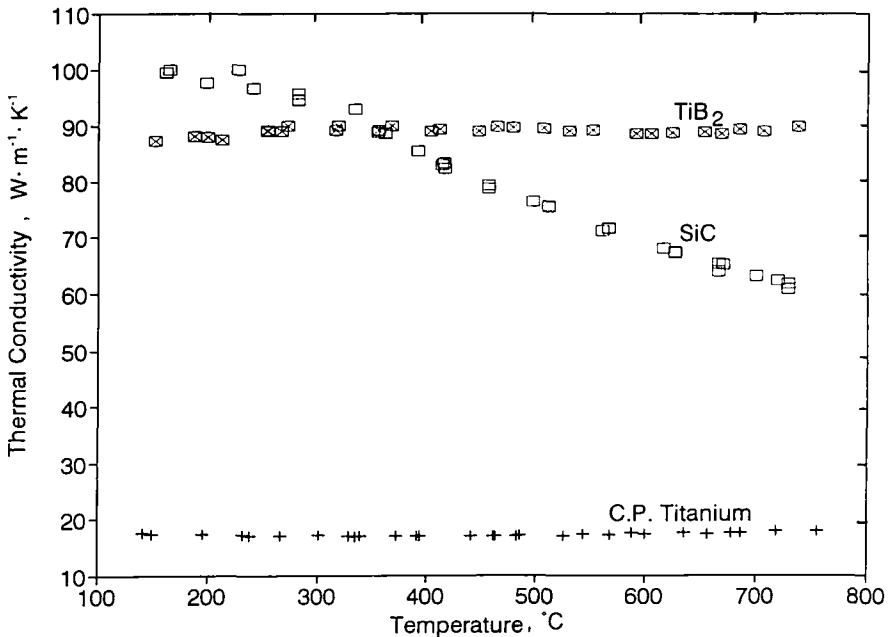


Fig. 1. Thermal conductivity data for SiC, TiB₂, and titanium.

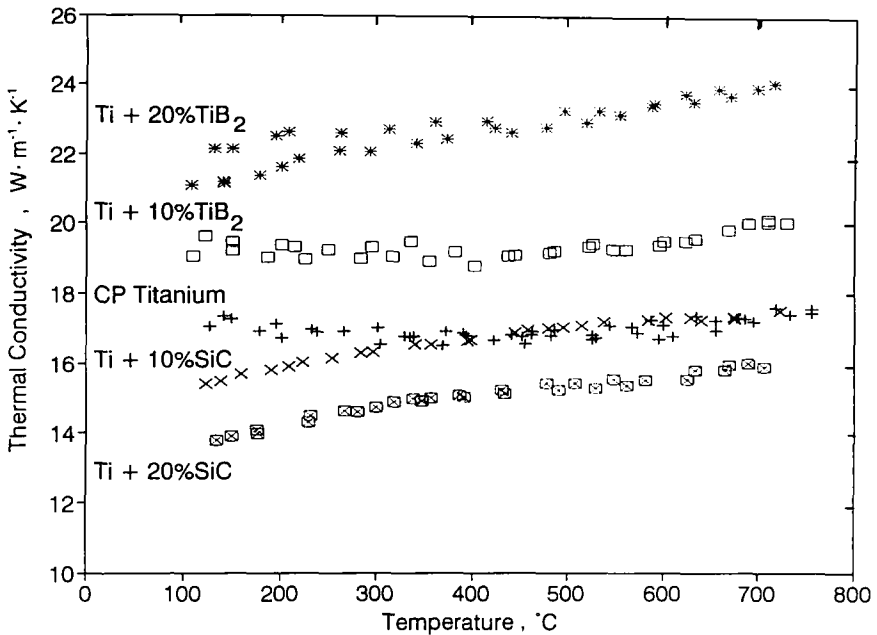


Fig. 2. Thermal conductivity data for unreinforced titanium and of Ti reinforced with 10 and 20% particulate SiC and TiB₂ composites.

than that of the unreinforced titanium and, moreover, decreases with increasing volume fraction of SiC reinforcement.

These results have been interpreted in terms of the thermal resistance of the reaction layers that exist between the matrix and two types of particulate reinforcements [6]. The reaction between Ti and SiC, to produce TiC and Ti₅Si₃, has been studied in some detail [7-12]. In a previous study of the Ti-SiC system [6], preliminary conductivity data were reported indicating poor interfacial contact, and it was noted that the reaction is accompanied by a relatively large volume change of -4.6%. This volume reduction will set up radial tensile stresses at the interface, opposing the differential thermal contraction stresses and tending to cause interfacial cracking. A reaction also takes place [13, 14] in the Ti-TiB₂ system, to form the monoboride, TiB, although the rate of the reaction is apparently slower than for Ti-SiC. It has also been reported [15, 16] that this reaction does not mechanically weaken the interface to the same degree as that in Ti-SiC. This may be a consequence at least partly of the much lower volume decrease accompanying the reaction, reported as -1.4%. Certainly the data reported here confirm that the interface in these as-

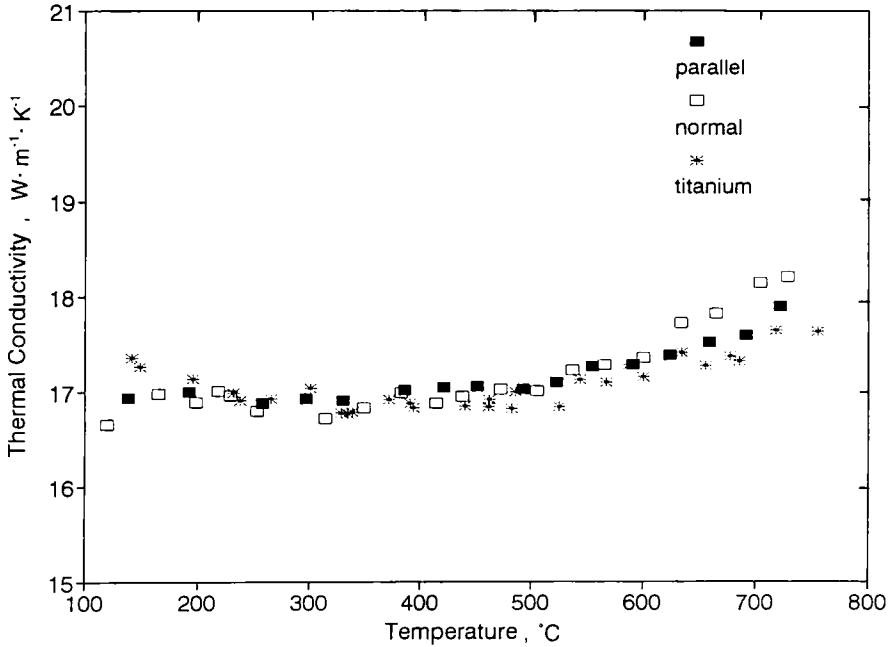


Fig. 3. Thermal conductivity data for pure titanium and Ti-10 (vol%) SiC short fibers, parallel and normal to the extrusion direction.

fabricated Ti-TiB₂ particulate composites has a higher thermal conductance than the Ti-SiC particulate composites.

Figure 3, shows the thermal conductivity data for the Ti-10 (vol%) SiC short fibers, for measurements made parallel and normal to the extrusion direction. The parallel and normal composite conductivities have similar values, the parallel conductivity slightly lower at higher temperatures. The short-fiber composites show little improvement over the unreinforced titanium.

3.2. Effect of Heat Treatment

Figure 4 shows the thermal diffusivity for Ti-20 (vol%) TiB₂ during an annealing cycle. Thermal diffusivity measurements were taken during heating to 950°C, at intervals while at temperature, and during cooling. The diffusivity measurements show a discontinuity at around 880°C corresponding to the α - β transformation in the titanium matrix. When the composite is held at 950°C there is an initial rise in the thermal diffusivity after ~10 min; it then falls off and a moderate decrease is observed. On subse-

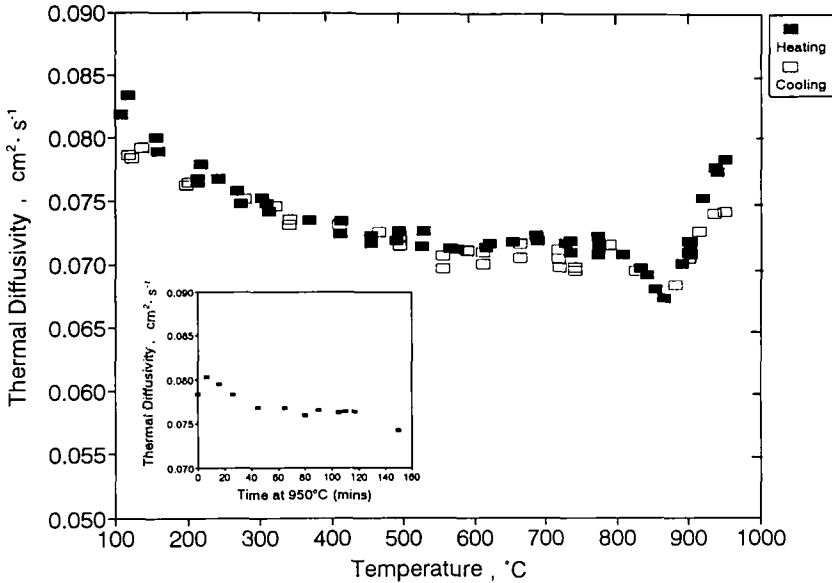


Fig. 4. Thermal diffusivity data for Ti-20 (vol%) TiB₂ during an annealing cycle.

quent cooling the thermal diffusivity remains relatively unchanged from that observed during heating. This result suggests that the reaction layer formed during heat treatment for 150 min at 950°C has not significantly impaired the thermal conductance.

The heat-treated composite Ti-20 (vol%) TiB₂ showed a slight increase in the thermal conductivity (Fig. 5) after heat treatment at 950°C for 40 min. This enhancement of thermal conductivity could be accounted for by two effects: (i) the interfacial thermal resistance between TiB₂ and the Ti may have been reduced as a result of the heat treatment; (ii) the volume fraction of TiB₂ plus reaction products increases as the reaction proceeds during heat treatment.

However, after a more substantial heat treatment, 21 h at 950°C, the thermal conductivity decreases to a value slightly below that of as extruded composite. This is believed to be attributed to the breakdown of the particulate/matrix reaction layer as a result of the larger volume of reaction product after the longer heat treatment. It should be noted that even after 21 h at 950°C the thermal diffusivity/conductivity of the Ti-20 (vol%) TiB₂ composite is greater than that of the unreinforced titanium despite the predicted interfacial damage around the particulates.

Figure 6 shows the thermal diffusivity for Ti-20 (vol%) SiC during an annealing cycle. The diffusivity measurements show a slight increase above 650°C, possibly attributable to microcrack closure at the matrix/particle

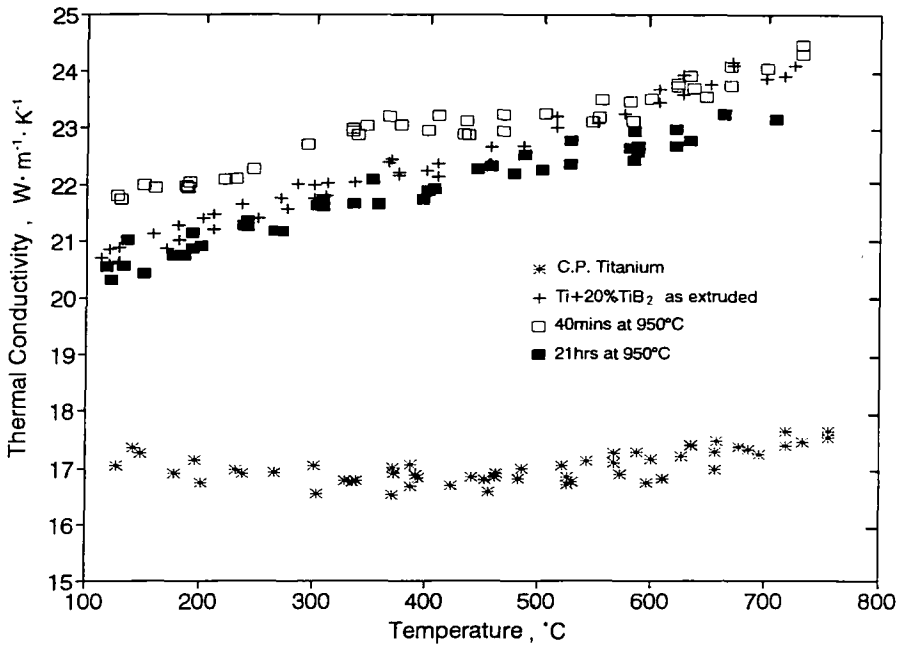


Fig. 5. Thermal conductivity data for Ti-20 (vol%) TiB₂ after heat treatment at 950°C.

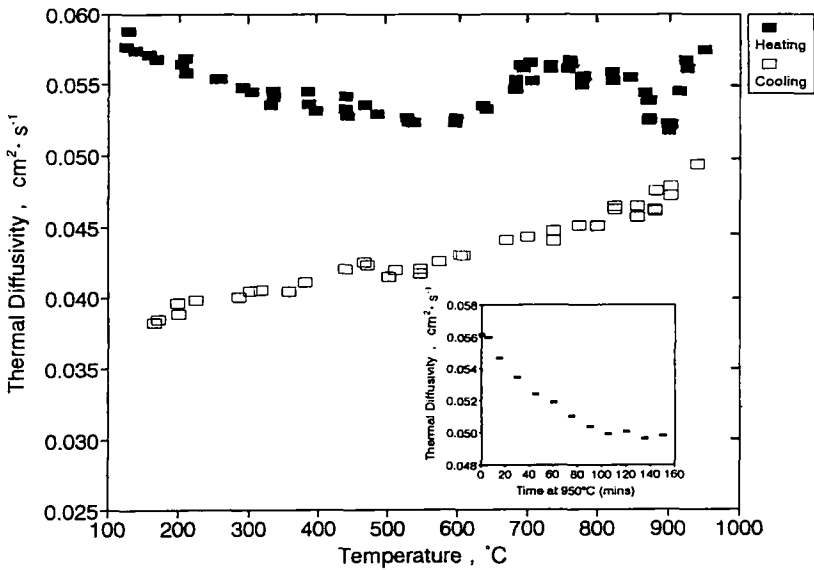


Fig. 6. Thermal diffusivity data for Ti-20 (vol%) SiC during an annealing cycle.

interfaces. A discontinuity is again observed around 880°C, corresponding to the α - β transformation in titanium. When the composite is held at 950°C, the thermal diffusivity decreases rapidly with time but begins to level off after ~100 min. On subsequent cooling, the thermal diffusivity continues to decrease to a value far below that shown by the heating data. This result suggests that the thermal conductance of the reaction layer formed during the time at temperature has been significantly impaired.

The effect of heat treatment on the Ti-20 (vol%) SiC composite is shown in Fig. 7. It can be seen that the already low conductivity of this composite is further depressed by heat treatment. It should be noted that a large decrease in conductivity is observed after heat treating for only 40 min at 950°C. Longer heat treatments produce only a slight reduction in the thermal conductivity. This is consistent with the observations in Fig. 6.

While the thermal properties of the reaction products may affect the thermal conductance, it seems unlikely that the difference in thermal conductivity of compounds concerned would be sufficiently different in this regard to explain the observed behavior. A more probable explanation lies in the degree of local microcracking, porosity, and general damage in the vicinity of the interface. This could explain the behavior of heat-treated Ti-20 (vol%) SiC, where a larger decrease in thermal conductivity is seen

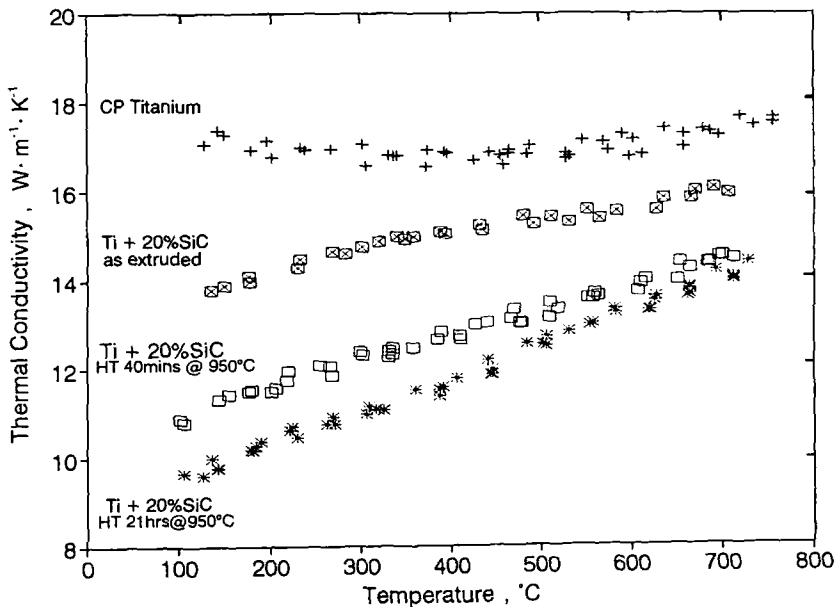


Fig. 7. Thermal conductivity data for Ti-20 (vol%) SiC after heat treatment at 950°C.

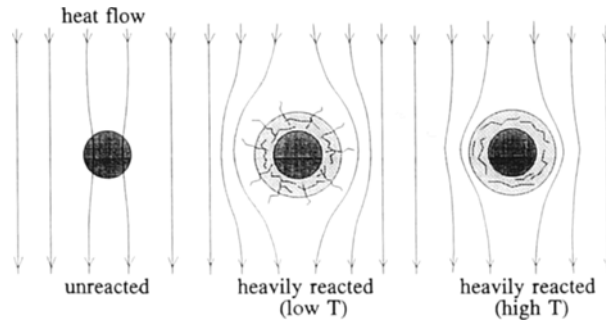


Fig. 8. Schematic illustration of the proposed nature of the heat flow around inclusions for the unreacted composite and for the reacted material at low and high temperatures.

at low temperatures where cracks offer high thermal resistance. At higher temperatures where crack closure occurs, the interfacial thermal resistance is reduced, resulting in a smaller decrease in thermal conductivity. This proposed effect is illustrated schematically in Fig. 8.

The experimental data can also be presented in the form of a ratio of the matrix conductivity (Fig. 9). This plot illustrates that the thermal resistance of the interface is high in the Ti-SiC system but low in the

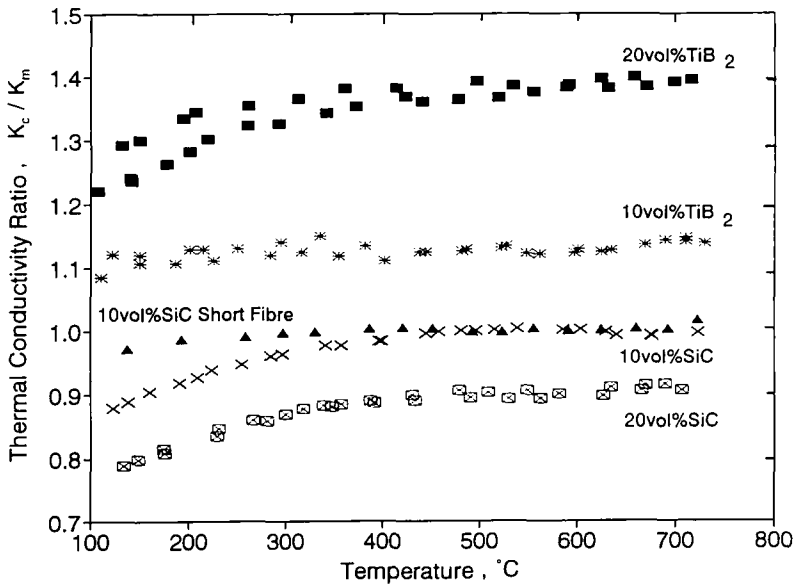


Fig. 9. The experimental composite thermal conductivity data presented in the form of a ratio of the matrix conductivity.

Ti-TiB₂ composites. It is the reacted/cracked interfaces within the Ti-SiC composites that are responsible for a high interfacial thermal resistance, thus lowering the thermal conductivity below that recorded for pure titanium. Furthermore, the nature of the proposed radial cracks round the particulates may explain why the effective decrease in thermal conductivity is reduced at higher temperatures, since differential thermal expansion stresses may act to close cracks and reduce the interfacial thermal resistance.

In order to analyze in detail the data shown in Fig. 9, it is useful to examine models for thermal conduction in composites which incorporate an interfacial thermal resistance. Such a thermal resistance is usually characterized by an interfacial heat transfer coefficient or thermal conductance, h ($\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$). For a volume fraction f of spherical particles (having a radius r) in a relatively dilute composite, an analytical expression given by Hasselman and Johnson [17] can be used to predict the conductivity of the composite K_c :

$$K_c = K_m \frac{[2f(K_p/K_m - K_p/rh - 1) + K_p/K_m + 2K_p/rh + 2]}{[f(1 - K_p/K_m + K_p/rh) + K_p/K_m + 2K_p/rh + 2]} \quad (3)$$

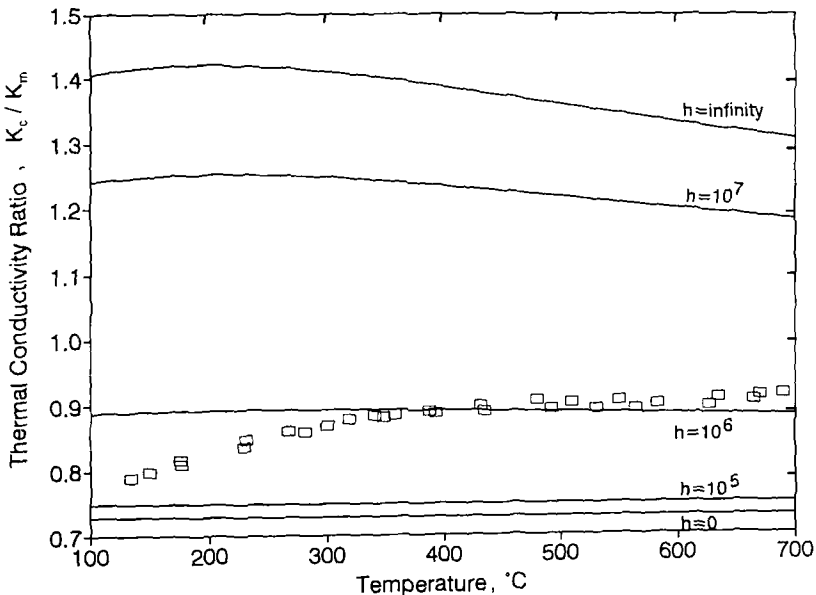


Fig. 10. Plots of the thermal conductivity ratio K_c/K_m for Ti-20 (vol%) SiC, against temperature, showing both experimental data and predictions from Eq. (3), based on several values for h (in $\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$) and using measured conductivities for both matrix and reinforcement.

where K_p and K_m are the conductivities of the particles and matrix, respectively. In Fig. 10, the experimental conductivity data for the Ti-20 (vol%) SiC composite have been plotted as ratios to that of the matrix. Also shown are predictions from Eq. (3) corresponding to several h values, using the experimental conductivity values for matrix and reinforcement, and a particle radius of $10\ \mu\text{m}$. It can be seen that these data are consistent with an h value of around $10^6\ \text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$, apparently rising somewhat with increasing temperature. This is a relatively small value for particle-matrix heat exchange in a system with particles of this size, and it can be seen from Fig. 10 that it represents behavior rather closer to an insulating interface ($h=0$) than to a perfect interface ($h=\infty$). If the analogous plots to those in Fig. 10 are plotted for the Ti-20 (vol%) TiB_2 system (Fig. 11), then the interfacial conductance is much higher and, at high temperatures, is consistent with perfect interfacial contact ($h=\infty$).

In general, this work has illustrated that TiB_2 -reinforced titanium has a significantly higher thermal conductivity than unreinforced titanium even after substantial heat treatment. In contrast SiC reinforced titanium has a

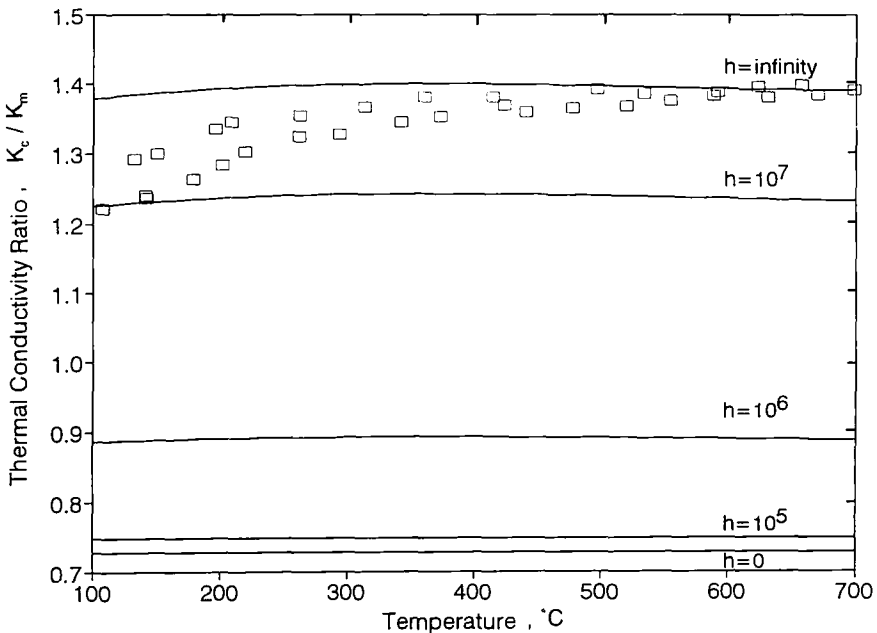


Fig. 11. Plots of the thermal conductivity ratio K_c/K_m for, Ti-20 (vol%) TiB_2 , against temperature, showing both experimental data and predictions from Eq. (3), based on several values for h (in $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$) and using measured conductivities for both matrix and reinforcement.

lower thermal conductivity than titanium, which decreases with further heat treatment. These increases and decreases in thermal conductivity are strongly dependent on the thermal conductance of the interfacial layer between the matrix and the reinforcement, which in turn depends on the interfacial chemistry and types of reactions.

4. CONCLUSIONS

The following conclusions can be drawn from this work.

(a) The thermal diffusivity/conductivity of extruded Ti-TiB₂ composites is significantly greater than that of the unreinforced matrix and is enhanced with increasing volume fractions of reinforcement.

(b) The thermal diffusivity/conductivity of the Ti-SiC composites is considerably lower than that of the unreinforced titanium and decreases with increasing volume fraction of SiC reinforcement.

(c) In the Ti-TiB₂ system, heat treatment causes initial increase in the thermal conductivity of the composite. Further heat treatment reduces the thermal conduction. The observed behavior is explained in terms of interfacial cracking and damage in the matrix-particle reaction layers caused by a 1.4% decrease in reaction production.

(d) In the Ti-SiC system any heat treatment decreases the composite thermal conductance. This is believed to be caused by the higher reaction rate and the larger accompanying volume change (~4.6%) taking place at the matrix-particle interface.

REFERENCES

1. W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbot, *J. Appl. Phys.* **32**:1679 (1961).
2. R. Taylor, *J. Phys. E. Sci. Inst.* **13**:1193 (1980).
3. L. M. Clark and R. E. Taylor, *J. Appl. Phys.* **46**:714 (1975).
4. R. D. Cowan, *J. Appl. Phys.* **34**:1679 (1962).
5. Y. S. Touloukian and E. H. Buyco, *Thermophysical Properties of Materials, Vols. 4-5* (IFI/Plenum, New York/Washington, DC, 1970), pp. 257-262 (vol. 4), pp. 378-389, 448-450 (Vol. 5).
6. A. J. Reeves, R. Taylor, and T. W. Clyne, *Mater. Sci Eng.* **141**:129 (1991).
7. A. J. Reeves, H. Dunlop, and T. W. Clyne, *Met. Trans.* **23**:970 (1991).
8. P. Martineau, M. Lahaye, R. Pailler, R. Naslain, M. Couzi, and F. Cruege, *J. Mater. Sci.* **19**:2749 (1984).
9. S. K. Choi, M. Chandrasekaran, and M. J. Brabers, *J. Mater. Sci.* **25**:1957 (1990).
10. C. G. Rhodes, A. K. Gosh, and R. A. Spurling, *Metall. Trans.* **18A**:2151 (1987).
11. M. Nathan and J. S. Ahearn, *Mater. Sci. Eng.* **A126**:225 (1990).
12. E. P. Zironi and H. Poppa, *J. Mater. Sci.* **16**:3115 (1981).
13. C. Jones, C. J. Kiely, and S. S. Wang, *J. Mater. Res.* **4**:327 (1989).
14. P. B. Prangell, A. J. Reeves, T. W. Clyne, and W. M. Stobbs, in *2nd European Conference on Advanced Materials and Processes, Euromat '91*, T. W. Clyne and P. J. Withers, eds. (Institute of Metals, Cambridge, 1992), pp. 215-229.

15. C. M. Warwick and J. E. Smith, in *12th Riso Symposium—Processing Microstructure & Properties of Metal Matrix Composites*, N. Hansen, ed. (Riso National Laboratory, Copenhagen, Denmark, 1990), pp. 735–742.
16. A. J. Reeves, W. M. Stobbs, and T. W. Clyne, in *12th Riso Symposium—Processing Microstructure & Properties of Metal Matrix Composites*, N. Hansen, ed. (Riso National Laboratory, Copenhagen, Denmark, 1991), pp. 631–639.
17. D. P. H. Hasselman and L. F. Johnson, *J. Compos. Mater.* **21**:508 (1987).