Carbon fiber reinforced tin-lead alloy as a low thermal expansion solder preform

C.T. Ho and D.D.L. Chung
Composite Materials Research Laboratory and Center for Electronic and Electro-Optic Materials, Furnas Hall, State University of New York, Buffalo, New York 14260

(Received 20 November 1989; accepted 15 February 1990)

Tin-lead (40 wt.% Pb) solder-matrix composites containing 8–54 vol.% continuous unidirectional copper plated carbon fibers were fabricated by squeeze casting for use as low thermal expansion solder preforms. The low thermal expansion greatly increased the thermal fatigue life for solder joints between materials with low thermal expansion coefficients. For example, for 29 vol.% fibers, the thermal expansion coefficient was 8×10^{-6}/°C (25–105 °C) in the direction parallel to the fibers compared to a corresponding value of 24×10^{-6}/°C for plain solder. The thermal fatigue life for cycling 2 cm long alumina-to-alumina solder joints between 25 and 100 °C was increased from 98 to 183 cycles by using 29 vol.% carbon fibers in the composite solder. The fibers also increased the tensile modulus and tensile strength of the solder, but the ductility was decreased. The copper coating on the carbon fibers increased the tensile strength and ductility of the composite.

I. INTRODUCTION

Solder preforms are used to join various parts of an electronic package. For example, they are used to join a ceramic cap and a multilayer ceramic substrate in a multichip module. Because the thermal expansion coefficient of a solder is in general much higher than that of a ceramic, the solder joint suffers from a poor resistance to thermal fatigue. Thus, there is a need for a solder with a low coefficient of thermal expansion.

Composite materials can be tailored to exhibit a chosen thermal expansion coefficient, as the filler species and the filler volume fraction can be judiciously chosen. For a low thermal expansion composite, the filler must have a low thermal expansion coefficient. Moreover, the filler should preferably be a good electrical conductor, because the soldered joint may serve as an electrical connection as well as a mechanical connection. It should also preferably be a good thermal conductor for heat dissipation from the electronic package. In addition, the filler should be wetted well by liquid solder in order to facilitate composite fabrication. A further requirement is that, upon remelting and solidification of the solder in the solder-matrix composite, the filler distribution in the composite remains uniform.

Molybdenum particles have been used as a filler in solder-matrix composites.[1] However, their distribution in the solder (Sn–40% Pb alloy) became nonuniform after remelting and solidification of the solder in the composite.[2] Thus, molybdenum is not a suitable filler in spite of its low coefficient of thermal expansion.

Carbon fibers have nearly zero thermal expansion coefficient. In contrast to ceramic fibers (which also have low thermal expansion coefficients), carbon fibers are a good electrical conductor and a good thermal conductor. Furthermore, carbon fibers are widely available in a continuous form, which makes them even more effective for lowering the thermal expansion coefficient of the composite and which prevents the fiber distribution from becoming nonuniform after remelting and solidification. Therefore, this paper uses continuous carbon fibers as the filler in solder.

Tin-lead alloys are most commonly used for solders. Carbon-fiber reinforced tin-lead alloys had been previously fabricated by liquid metal infiltration for bearing applications[3] and by investment casting for fundamental process study.[4] For both methods, the carbon fibers were electroplated with copper in order to ensure good wetting of the fibers by the alloy.[3,4] Carbon-fiber reinforced tin (containing 7.5 wt.% Sb and 3.5 wt.% Cu) had also been previously fabricated by squeeze casting for fundamental process study.[5] In this case, the carbon fibers were electroplated with nickel in order to avoid the oxidation of the fibers during casting.[5] This paper provides the first study of carbon fiber reinforced metals for solder applications. Following Refs. 3 and 4, copper-plated carbon fibers were used in this work.

II. COMPOSITE FABRICATION

The solder alloy used contained 60 wt.% Sn and 40 wt.% Pb, as this is the most commonly used solder composition. The solidus of this alloy is 183 °C; the liquidus is about 192 °C.

The filler used was continuous copper coated carbon fibers. The fibers were pitch-based (Amoco's Thornel

P-100), with a diameter of 10 μm, a tensile modulus of 690 GPa, a tensile strength of 2400 MPa, and a tensile ductility (elongation) of 0.3%. The copper coating was slightly more than 1 μm thick. The coated carbon fibers were kindly provided by American Cyanamid Company. Uncoated and unsized fibers (Amoco's Thornel P-100) were also used for the sake of comparison.

The carbon-fiber reinforced solder was prepared by squeeze casting, using a mold cavity of length 6 cm and width 1.2 cm. After placing carbon fibers of length 5 cm unidirectionally along the length of the mold cavity, a small amount of dilute hydrochloric acid was poured into the mold. (The acid treatment was for the purpose of activating the surface of the uncoated fibers for better bonding to the matrix, but it was applied to both coated and uncoated fibers for consistency.) Then the temperature of the mold was raised to 150 °C in order to cause the acid to evaporate. After that, liquid solder heated to 400 °C was poured into the mold maintained at 150 °C, and pressure ranging from 30 to 50 MPa was immediately applied through a piston at the top of the mold. The pressure was maintained for 10 min while the mold was allowed to cool to near room temperature.

III. COMPOSITE CHARACTERIZATION

Solder-matrix composites containing various volume fractions of carbon fibers were characterized in terms of their tensile properties and thermal expansion coefficients.

A. Tensile properties

Tensile tests were performed on composites containing copper-coated carbon fibers as well as those containing uncoated carbon fibers. The tests were carried out using a hydraulic Materials Testing System (MTS). The strain was measured by using a strain gage (Measurements Group, Inc., gage type EA-13-120LZ-120, resistance = 120.0 (±0.3%) ohms, gage factor = 1.095 ± 0.5% at 75 °F). The tensile stress was applied along the fiber direction. The gage length was 4.16 cm.

Figures 1–3 show the tensile modulus, tensile strength, and tensile ductility (elongation) as functions of the volume fraction of fibers in the composite solder. The modulus and strength increased with increasing fiber content, while the ductility decreased with increasing fiber content, as expected. The strength and ductility were higher for composites containing copper-coated carbon fibers than for those containing uncoated fibers. This is consistent with the improved wetting between the matrix and fiber due to the copper coating. The modulus was not affected by the copper coating, as expected.

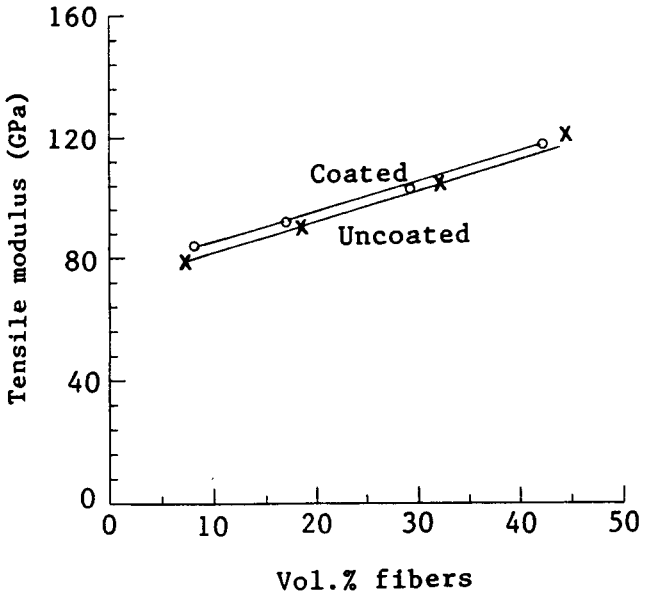


FIG. 1. Tensile modulus versus fiber content. Data for copper coated carbon fibers are shown by circles; those for uncoated carbon fibers are shown by crosses.

B. Thermal expansion coefficient

The thermal expansion coefficients of composites containing 8 to 42 vol.% copper coated carbon fibers were measured at 25–105 °C parallel and perpendicular to the fiber direction. Prior to the measurement, the specimens were annealed in vacuum at 150 °C for 2 h and then allowed to cool to room temperature. The

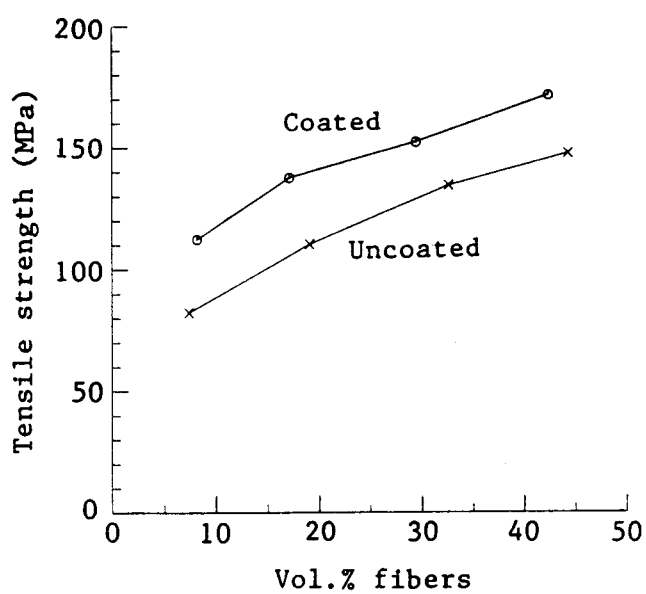


FIG. 2. Tensile strength versus fiber content. Data for copper coated carbon fibers are shown by circles; those for uncoated carbon fibers are shown by crosses.

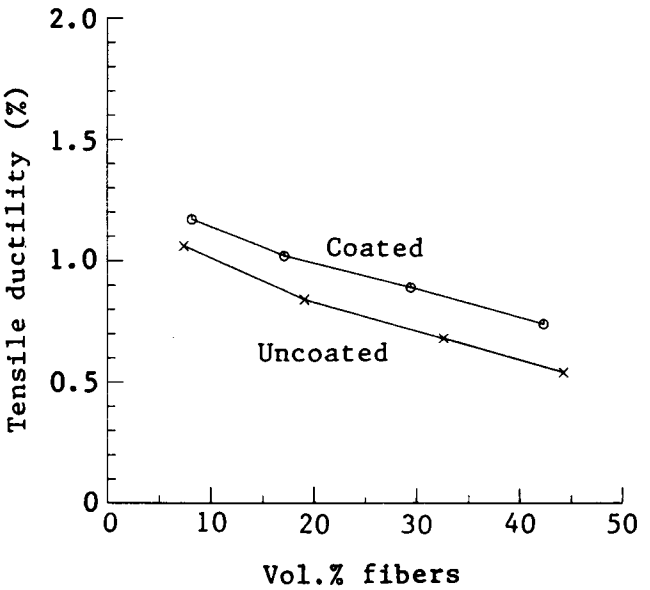


FIG. 3. Tensile ductility (elongation) versus fiber content. Data for copper coated carbon fibers are shown by circles; those for uncoated carbon fibers are shown by crosses.

measurements were made using a Mettler TMA40 Thermal Mechanical Analyzer operated at a heating rate of 10 °C/min.

Table I shows the thermal expansion coefficients. The values parallel to the fibers were lower than the corresponding ones perpendicular to the fibers. For each orientation, the coefficient parallel to the fibers decreased markedly with increasing fiber content, while the coefficient perpendicular to the fibers decreased much less with increasing fiber content. The coefficient parallel to the fibers even reached values close to zero at fiber contents above 42 vol.%. The coefficient increased with increasing temperature for a given fiber content and a given orientation.

IV. SOLDER BOND TESTING

A. Bonding process

The ability of the solder composites containing copper-coated carbon fibers to bond together materials of low thermal expansion coefficients was tested. The materials chosen included a ceramic (alumina or Al_2O_3, electronic grade, thermal expansion coefficient = 6.7×10^{-6}/°C at 25 °C) and a metal alloy (Kovar or Fe–29% Ni–17% Co, thermal expansion coefficient = 5.3×10^{-6}/°C at 25 °C). In order to promote wetting by the solder, the bonding surface of each of these materials was coated with a thin film of gold (20–40 Å thick) by vacuum evaporation.

The composite samples used were of length 2 cm (along the fiber direction), width 1.2 cm, and thickness 0.58 cm. The alumina and Kovar had thicknesses 0.102 and 0.025 cm, respectively.

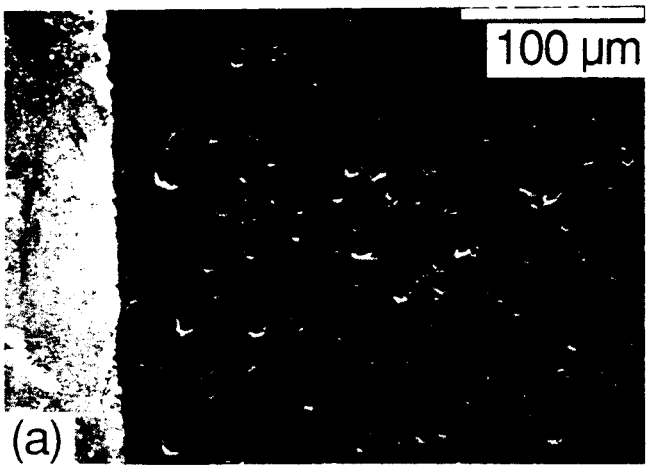
Solder joints between two sheets of alumina and between a sheet of alumina and a sheet of Kovar were made by hot-pressing the composite solder between the two sheets to be joined at 180 °C and 500 psi (4 MPa) for 20 min. Even though 180 °C is just below the solidus temperature, the solder at the surface of the composite did melt during the heating. This slight melting was necessary for bonding. Joints of a similar quality could be made at temperatures above the solidus temperature. In particular, a joint was made between alumina pieces at 187 °C, at which partial melting of the solder occurred. In spite of the partial melting, the carbon fiber (copper-coated or not) distribution remained unchanged by the melting and subsequent solidification.

B. Microstructure

Figure 4 shows scanning electron microscope (SEM) photographs of polished cross sections of (a) the solder (0 vol.% fibers)-alumina interface, and (b) the

TABLE I. Thermal expansion coefficients of solder-matrix composites containing various volume fractions of copper coated carbon fibers, in directions parallel (∥) and perpendicular (⊥) to the fibers.

Vol.% fibers	Direction	Thermal expansion coefficient (10^{-6}/°C)								
		25 °C	35 °C	45 °C	55 °C	65 °C	75 °C	85 °C	95 °C	105 °C
8.2	∥	10.42	11.37	12.16	13.09	14.23	15.10	15.94	16.23	16.98
	⊥	18.32	19.47	20.11	21.42	22.37	22.90	23.42	24.78	25.32
17.12	∥	8.43	8.90	9.24	9.79	10.21	11.80	12.72	13.41	14.10
	⊥	17.39	18.00	18.47	19.41	20.83	21.74	22.71	23.62	24.83
29.42	∥	4.31	4.90	5.70	6.92	7.91	8.42	9.53	10.43	11.84
	⊥	16.80	17.80	18.32	19.11	20.52	20.99	21.43	22.84	24.12
42.37	∥	0.62	0.74	0.92	1.10	1.14	1.20	1.27	1.36	1.47
	⊥	15.93	16.24	17.32	18.42	18.99	19.92	21.11	22.10	23.8
54.1	∥	−0.89	−0.80	−0.64	−0.64	−0.64	−0.62	−0.60	−0.62	−0.62



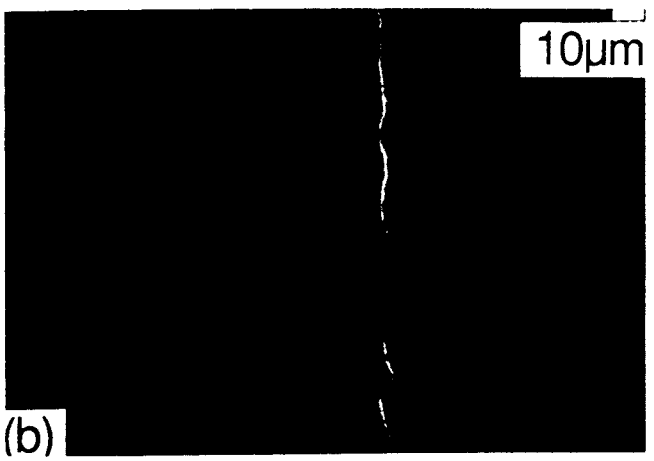
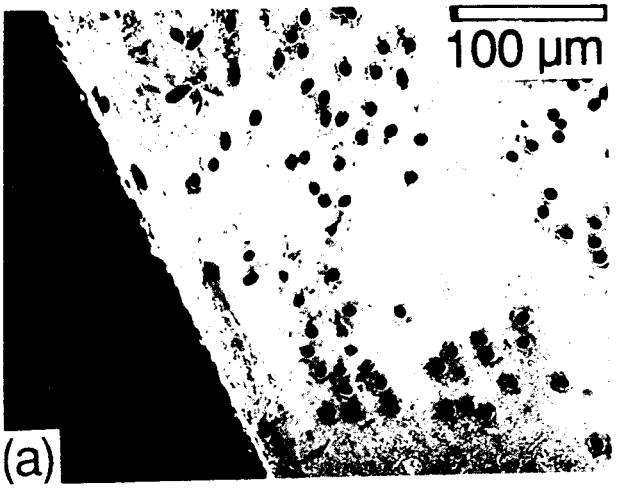


FIG. 4. SEM photographs of polished cross sections of (a) the solder (0 vol.% fibers)-alumina interface (with the solder at the left side of the interface), and (b) the solder (0 vol.% fibers)-Kovar interface (with the solder at the right side of the interface).



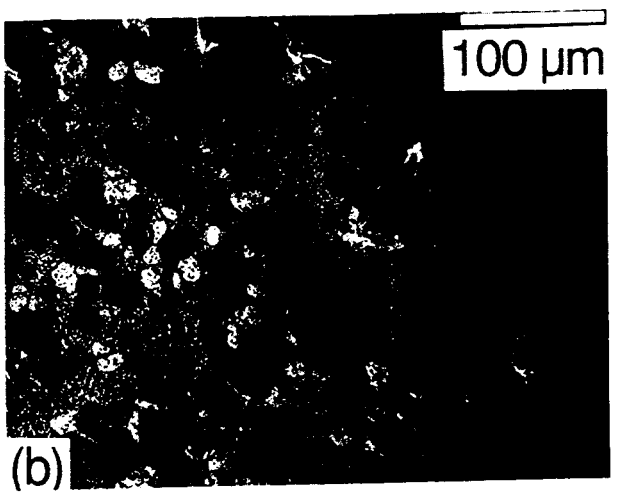


FIG. 5. SEM photographs of polished cross sections of (a) the composite (17.12 vol.% fibers)-alumina interface (with the composite at the right side of the interface), and (b) the composite (17.12 vol.% fibers)-Kovar interface (with the composite at the left side of the interface).

solder (0 vol.% fibers)-Kovar interface. No void or crack was observed between the solder and the alumina or Kovar.

Figure 5 shows SEM photographs of polished cross sections of (a) the composite (17.12 vol.% fibers)-alumina interface, and (b) the composite (17.12 vol.% fibers)-Kovar interface. The composite was viewed in the direction of the fibers in each photograph. The tip of each carbon fiber appeared as a black circle surrounded by a halo, which was due to the reaction of the copper coating with the solder alloy matrix. The reaction products were presumably the ternary equivalents of the phases Cu_3Sn and Cu_6Sn_5.[3] The matrix consisted of two microconstituents, namely a proeutectic phase (white patches) and a eutectic solid. No void or crack was observed between the composite solder and the alumina or Kovar.

C. Thermal fatigue testing

The ability of the solder bond to withstand thermal cycling between room temperature and 100 °C was investigated by observing the solder joints under an optical microscope after every cycle to look for the start of debonding (i.e., slight cracking between the solder composite and Al_2O_3 or between the solder composite and Kovar). The thermal cycling was carried out by alternating between furnace heating at 100 °C for 25 min and room temperature equilibration for at least 30 min.

Table II shows the thermal fatigue life (i.e., the number of cycles for debonding to start) for each composite composition and for each of two pairs of joined materials. The thermal fatigue life was longest for an intermediate fiber content of 29.42 vol.% for both pairs

TABLE II. Thermal fatigue life of alumina-to-alumina solder joints and alumina-to-Kovar solder joints for various volume fractions of copper coated carbon fibers in the composite solder.

Joint	Vol. % fibers	Fatigue life (cycles)
Alumina-to-alumina	0	98 ± 3
	8.2	104 ± 4
	17.12	149 ± 2
	29.42	183 ± 9
	42.37	91 ± 1
	54.1	81 ± 6
Alumina-to-Kovar	0	112 ± 1
	8.2	119 ± 2
	17.12	178 ± 8
	29.42	210 ± 12
	42.37	107 ± 4
	54.1	96 ± 3

of joined materials. This is reasonable because the thermal expansion coefficient parallel to the fiber direction was closest to the values of Al_2O_3 and Kovar for a fiber content of 29.42 vol.%, as shown in Table I.

Figure 6 shows optical microscope photographs of (a) the solder composite (8.2 vol.% copper coated carbon fibers)-alumina interface and (b) the solder composite (8.2 vol.% copper coated carbon fibers)-Kovar interface, just after the start of debonding. Each photograph shows a crack along the interface.

V. CONCLUSION

A tin-lead (40 wt.% Pb) solder-matrix composite preform containing continuous and unidirectional copper coated carbon fibers was developed. By varying the volume fraction of carbon fibers in the composite, we can control the thermal expansion coefficient all the way to zero. For example, for 29 vol.% fibers, the thermal expansion coefficient was 8×10^{-6}/°C (25–105 °C) in the direction parallel to the fibers, compared to a corresponding value of 24×10^{-6}/°C for plain solder. The thermal fatigue life was determined by thermal cycling between 25 and 100 °C and counting the cycles needed for debonding to start, as revealed by optical microscopy. For the composite containing 29 vol.% fibers, the thermal fatigue life of a 2 cm long alumina-to-alumina solder joint was 183 cycles, compared to a life of 98 cycles for a joint made with plain solder. Hence, the thermal fatigue life was increased by 87%. In addition, the fibers increased the tensile modulus and tensile strength of the solder, and are therefore expected to increase the creep resistance also.

The solder composites were successfully made by squeeze casting for copper-coated carbon fibers as well as the uncoated fibers. However, copper-coated carbon fibers are preferred because they resulted in composites

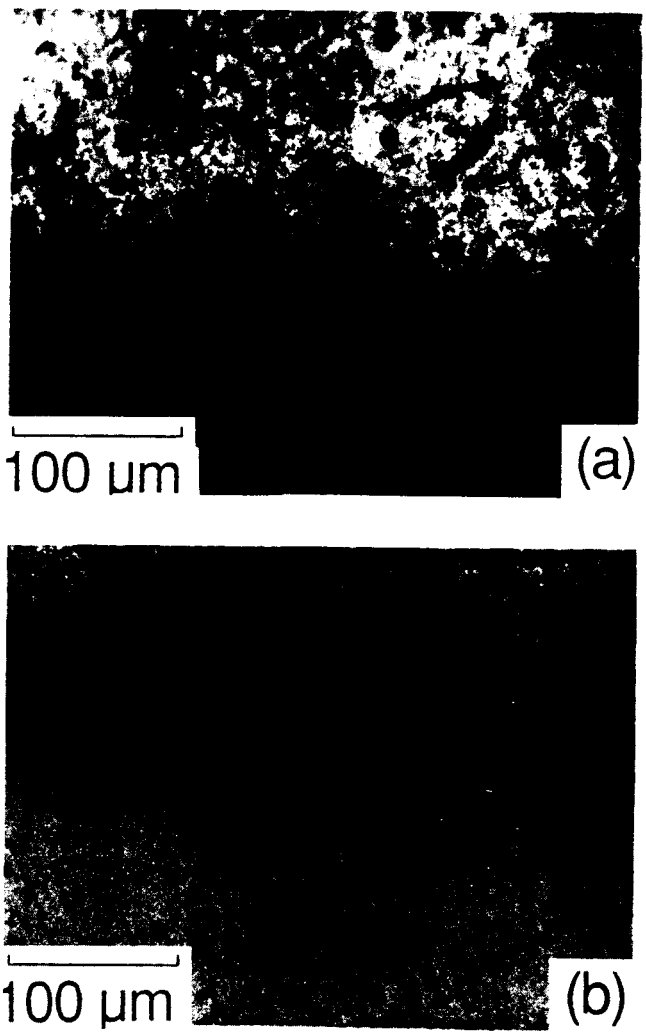


FIG. 6. Optical micrographs of (a) the composite (8.2 vol.% fibers)-alumina interface (with the composite at the upper side of the interface), and (b) the composite (8.2 vol.% fibers)-Kovar interface (with the composite at the upper side of the interface), just after the start of debonding.

that were higher in tensile strength and ductility. This effect of the copper is associated with the fact that copper improves the wetting of the fibers by the solder liquid.

ACKNOWLEDGMENT

Support from Nebo Corporation is acknowledged.

REFERENCES

[1]IBM Technical Disclosure Bulletin **29** (4), 1573 (1986).
[2]Shy-Wen Lai and D.D.L. Chung (unpublished results).
[3]C.F. Old, I. Barwood, and M.G. Nicholas, Pract. Met. Compos., Spring Meet., B47-B50, London, England, Inst. Metall. (1974).
[4]A. Miyase and K. Piekarski, Adv. Res. Strength Fract. Mater., 4th Int. Conf. Fract., 1977, edited by David M.R. Taplin (Pergamon, Elmsford, NY, 1978), Vol. 3B, pp. 1067–1071.
[5]David G. Gelderloos and Keith R. Karasek, J. Mater. Sci. Lett. **3**, 232 (1984).