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GRAPHITE/COPPER ALLOY INTERFACIAL ENERGIES DETERMINED USING THE SESSILE DROP METHOD

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ABSTRACT

Graphite surfaces are not wet by pure copper. This lack of wetting has been responsible for a debonding phenomenon that has been found in continuous graphite fiber/copper matrix composite materials subjected to elevated temperatures. By suitably alloying copper, its capability to wet graphite surfaces can be enhanced. In situ measurements of graphite/copper alloy wetting angles have been made using the sessile drop method. Interfacial energy values have been calculated based upon these measurements.

INTRODUCTION

Continuous fiber reinforced graphite/copper (Gr/Cu) composites offer potential for improved performance as high heat flux structures for elevated temperature applications requiring high thermal conductivity. These composites are candidate materials for applications such as space power radiator panels and as leading edge and engine heat exchanger materials for hypersonic aircraft. Gr/Cu composites made from pitch-based fibers possess a high thermal conductivity equivalent to copper. They also exhibit a high modulus of elasticity equivalent to beryllium, and moderate density similar to titanium [1].

The fabrication and performance of composite materials designed for elevated temperature applications is strongly influenced by the fiber matrix interface. A key aspect of metal/ceramic interfaces is the metal/ceramic interfacial energy. However, often the ideal fiber/matrix combinations, based upon their mechanical and physical properties, have high interfacial energies [2]. The high interfacial energies relative to the surface energies of the fibers results in a lack of wetting between the metals and fibers. This intrinsic lack of wetting causes difficulties in production of the composites, as shown in Figure 1. More importantly, the lack of wetting can lead to matrix fiber debonding and pore formation during the service life of the composites at elevated temperatures [1, 3].

Wettability studies using the sessile drop method have been conducted for the Gr/Cu system. Many investigators have noted that pure Cu does not wet Gr. Mortimer and Nicholas [4] have reported that small additions of Cr reduce the contact angle formed by Cu on HX30 Gr and vitreous carbon and that small additions of V reduce the contact angle on vitreous carbon in studies conducted in vacuum. Nogi et al. [5] have conducted similar experiments in an Ar-5H$_2$ atmosphere on single crystal Gr. They have concluded that Gr is wet by Cu-Cr alloys when the Cr content is high enough to create a continuous Gr/Cu-Cr interface. Kishkoparov et al. [6] conducted sessile drop tests in helium between 1250 and 1550°C using Gr powder. The alloying

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additions investigated include Fe, Co, Al, Ni and Sn. They have reported that alloys with more than 10% Fe or Co, and more than 3% Al wet Gr powder. The trends indicated by these studies are similar, but there are variations in the data due to the differences in materials and experimental techniques.
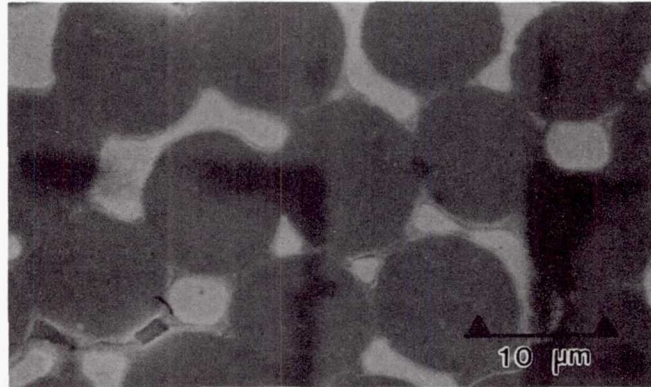

Figure 1. Copper 50 v/o P100 graphite fiber composite.

An experimental program has been conducted to assess the effect of alloying additions to Cu on the wetting angle established between the Cu-alloys and the polished surfaces of monolithic Gr utilizing a sessile drop technique. The alloying elements chosen are those which have limited solubility in solid Cu and are potential carbide formers. Most of the alloying elements chosen tend to strongly segregate to interfaces. Because the Gr/Cu composites are being considered for thermal conductivity applications, the additions of alloying elements were minimized with the intention of minimizing the thermal conductivity decrease. For this reason, an effective alloying addition is defined as one that produces the greatest decrease in contact angle, from that of pure Cu, for the lowest atomic percent addition.

EXPERIMENTAL PROCEDURE

Nominal additions of 0.5 at% and 1.0 at% of Cr, Fe, Hf, La, Mn, Nb, Si, Ta, Ti, V, Y and Zr were alloyed with Cu to produce alloys for sessile drop evaluation. Tests were also run using pure Cu as a standard.

Sessile drop tests were conducted in a 1 atm argon atmosphere. For each alloy, two to five individual tests were run on separate occasions. Commercial grade H-490 Gr discs of 2.54 cm diameter were polished to a 1 μm finish and placed directly on the pancake induction coil of the furnace. A Cu-alloy test specimen of 1.27 cm diameter was placed on top of the Gr. Temperatures were monitored using a two wavelength optical pyrometer measuring the temperature of the Gr substrate. To minimize the thermal gradient the Gr was surrounded by Al_2O_3 insulation. Separate tests with thermocouples indicated the thermal gradient between the Gr and Cu was $\leq$ 5°C.After achieving a vacuum $< 4.6 \times 10^{-3}$ Pa, the furnace was back-filled with argon. This procedure was repeated to allow additional flushing of the system. The Cu alloy and the Gr were simultaneously heated to the melting point of the alloy. The test temperature was then raised to a 50°C superheat and held for 3600 s. The test was recorded on videotape while the temperature was recorded on a strip chart recorder. The contact angles were measured at 300 s intervals during the test using a video monitor .

The angle measurements obtained were used in the Young-Dupre equation in order to calculate the Gr/Cu interfacial energies. For Gr/Cu, the Young-Dupre equation is as follows:

$$\gamma_{Gr/Cu} = \gamma_{Gr/v} - \gamma_{Cu/v} \cos\theta \qquad (1)$$

where $\gamma_{Gr/Cu}$ is the Gr/Cu interfacial energy, $\gamma_{Gr/v}$ is the free surface energy of Gr, $\gamma_{Cu/v}$ is the free surface energy of Cu and θ is the wetting angle.

RESULTS

Chemical Analysis

The compositions of the alloys tested, their oxygen contents and the amount of addition not tied up as an oxide are listed in Table 1. The chemical analyses of these alloys indicate considerable variation from the intended targets of 0.5 at% and 1.0 at% due to difficulties encountered in melting.

Table 1. Chemical composition of copper alloys

Alloy no.	Addition	wt%	at%	O, ppm	Available addition, at%
1	Si	0.3	0.68	49	0.671
2	Si	0.4	0.90	12	0.898
3	Ti	0.041	0.054	27	0.049
4	Ti	0.041	0.054	658	-0.076
5	V	0.3	0.37	34	0.357
6	V	0.8	1.00	57	0.977
7	Cr	0.4	0.49	10	0.487
8	Cr	0.5	0.61	66	0.593
9	Cr	0.8	0.98	13	0.977
10	Cr	0.9	1.10	16	1.106
11	Cr	1.0	1.22	11	1.217
12	Mn	0.4	0.46	26	0.45
13	Mn	0.9	1.04	10	1.036
14	Fe	0.1	0.11	16	0.104
15	Fe	0.4	0.45	10	0.446
16	Y	0.2	0.14	37	0.13
17	Y	0.2	0.14	404	0.033
18	Zr	0.1	0.07	10	0.068
19	Zr	0.4	0.28	295	0.222
20	Nb	0.2	0.14	34	0.127
21	La	0.038	0.017	20	-0.002
22	Hf	1.0	0.36	46	0.351
23	Hf	2.0	0.72	254	0.669
24	Ta	0.3	0.11	20	0.107
25	Ta	0.4	0.14	76	0.128
26	Ta	0.8	0.28	18	0.277

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Contact/Wetting Angle Measurements

Photographs of the test specimens were taken from each of the videotapes. An example is shown for pure Cu in Figure 2. Contact angle data as a function of alloying element are given in Table 2. The values reported are for the equilibrium angle. Most alloys reached equilibrium within 100 s after melting. Based on all the measurements, a pooled standard deviation for the contact angle measurements was calculated to be 16°. The scatter due to the optical measurement system is much less than this value. The major source for error is believed to be the presence of surface oxide on the Cu-alloy test specimen. The kinetics of oxide film formation on the Cu-alloy free surface varies for each alloying element, and therefore the stability of the surface oxide also varies. Additions of Cr, Hf, V, Y and Zr significantly decrease the wetting angle from that of pure Cu. As indicated in Table 2, additions of less than 0.1 at% La or Ti result in a slightly decreased contact angle, whereas much greater additions of many of the other alloying elements are needed to produce the same effect. The contact angle measurements as a function of Cr addition are given in Figure 3. By increasing the amount of Cr addition, the contact angle of the Cu alloy on Gr can be reduced. The results for the Cu-Cr alloys correspond to those found by others [4, 5, 7].
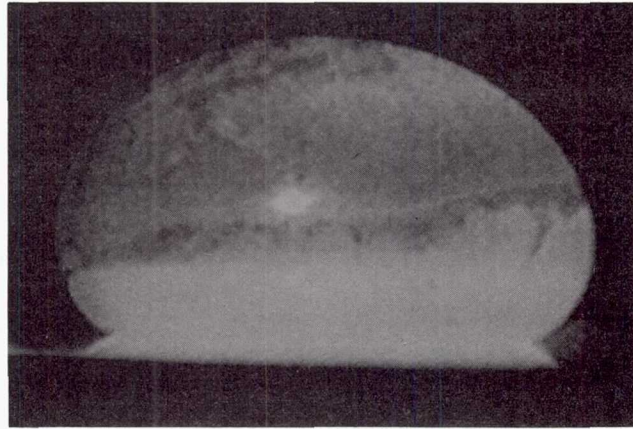

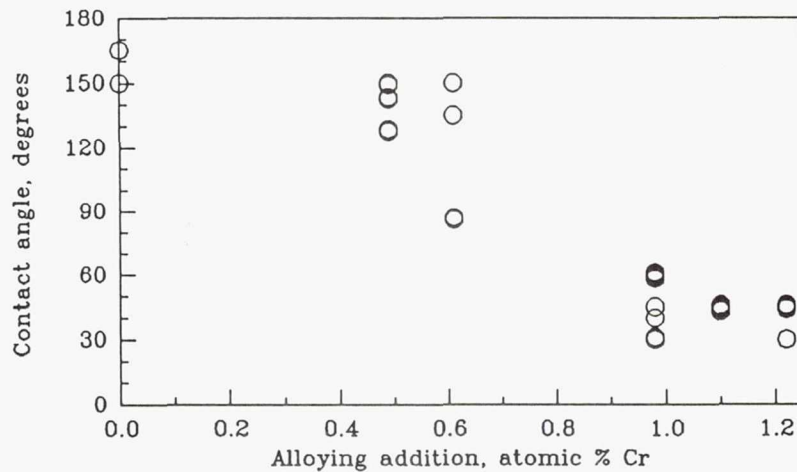Figure 2. Sessile drop test specimen. Pure copper: average contact angle 157°.

Figure 3. Contact angle as a function of Cr Addition.

Table 2. Graphite/Cu-alloy interfacial energy

Cu-alloy addition	at%	contact angle	$\gamma_{Gr/Cu}$ mJ/m^2	Cu-alloy addition	at%	contact angle	$\gamma_{Gr/Cu}$ mJ/m^2
Cu		157	1975	Fe	0.11	146	1858
					0.45	135	1702
Si	0.68	157	1975				
	0.90	150	1906	Y	0.14	111	1256
					0.14	144	1833
Ti	0.054	128	1585				
	0.054	119	1418	Zr	0.07	113	1298
					0.28	111	1256
V	0.37	128	1585				
	1.00	45	-106	Nb	0.14	140	1778
Cr	0.49	140	1778	La	0.017	138	1748
	0.61	114	1318				
	0.98	60	159	Hf	0.36	90	798
	1.10	45	-106		0.72	80	576
	1.22	41	-167				
				Ta	0.11	130	1620
Mn	0.46	142	1858		0.14	132	1654
	1.04	135	1702		0.28	142	1806

Gr/Cu Interfacial Energy Calculations

Using the Young-Dupre equation and assuming values for the free surface energy of Cu and the free surface energy of Gr, estimates of the Gr/Cu interfacial energy can be made. Values of 1279 mJ/m^2 for the Cu [8, 9] and 798 mJ/m^2 for the Gr [4] were used in the calculations. The value for Cu was assumed to be constant with alloying level. Interfacial energy values are listed in Table 2 for the Cu-alloys.

Some degradation of Gr surfaces, indicated by discoloration found in the areas not covered by the Cu-alloy test specimens, was observed. This may indicate some reaction was occurring at the Gr surface which may change the value of $\gamma_{Gr/v}$.

Scanning Electron Microscopy

Initial studies of the Gr/Cu-Cr interface have been conducted using the scanning electron microscope. In the case of Cu-1.22 at%Cr, which wets and adheres to the Gr, a 3 μm thick reaction layer forms at the interface as shown in Figure 4a. Energy dispersive spectroscopy (EDS) analysis indicates that this is a Cr-rich layer as shown in Figure 4b.

DISCUSSION

Wetting Angle Measurements

The wetting angle measurements given in Table 2 indicate that La is most effective in reducing the wetting angle per at% added, followed by Ti and Zr. Other elements that reduced the wetting angle significantly include Cr, Hf, V and Y. All of the alloys melted within 50°C of the melting temperature of pure Cu. However, the V alloys required a temperature of 1530°C to achieve a completely liquid state. While microscopy of the interfaces has not been completed, it is believed that these alloying elements segregated to the Gr/Cu interface and formed a reaction layer, most likely a carbide layer. The degree of wetting is also believed to be affected by whether the carbide layer is continuous or discontinuous as discussed by Nogi et al. [5]. Analysis of the Cu-Cr alloy interfaces, such as the one shown in Figure 4a, confirm that the best wetting is obtained when a continuous Cr carbide layer forms. Confirmation of the reaction layers and their compositions by optical microscopy and SEM examination is currently ongoing.

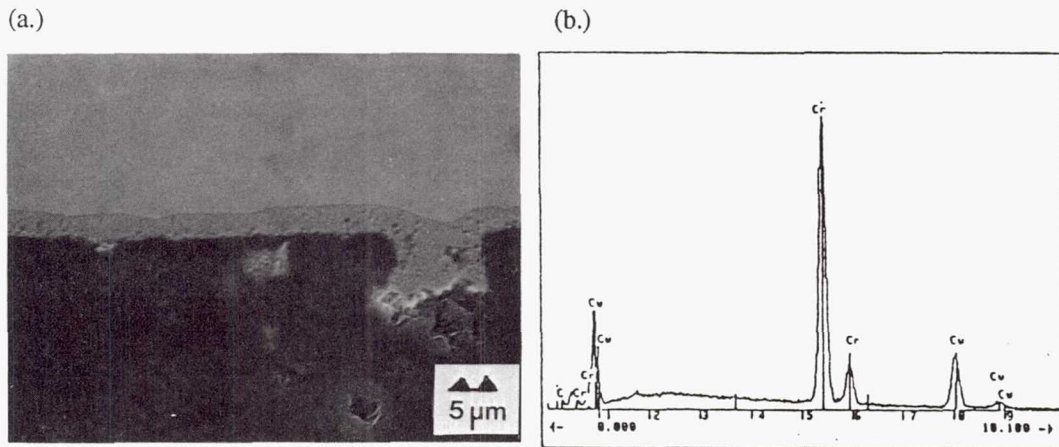(a.)   (b.)

Figure 4. (a.) SEM micrograph. Cu-1.22 at% Cr sessile drop test specimen: reaction layer approximately 3 μm. (b.) EDS spectrum from reaction layer.

Gr/Cu Interfacial Energy Calculations

The Gr/Cu interfacial energy was observed to be affected by alloying addition. The alloying elements most effective in lowering the Gr/Cu interfacial energy are La, Ti and Zr. The value calculated for pure Cu of 1975 mJ/m^2 is decreased to 1418 mJ/m^2 for an addition of only 0.054 at% Ti and to 1298 mJ/m^2 for 0.07 at% Zr. The Gr/Cu interfacial energy is also affected by the amount of alloying element present. As seen in Table 2, increasing at% of all the additions studied, with the exception of Ta, results in a greater decrease in interfacial energy.

The results of the calculations for the Gr/Cu interfacial energies shown in Table 2 indicate that, in some cases, such as with Cr and V, negative values can be obtained. These values are obviously incorrect. Three possible explanations exist for this discrepancy.

The first two possibilities concern the assumptions about the surface energies of the Cu and Gr. The surface energy of the Cu was assumed to be constant with respect to both alloying element and the amount of alloying element added. This assumption is probably not valid given the high mobility of the alloying elements in the liquid Cu and the tendency of many of the elements to segregate to interfaces. The presence of these alloying addition atoms at the Cu/vapor interface could decrease the surface energy to values considerably below the assumed value of 1279 mJ/m^2.

The assumption that the surface energy of Gr is 798 mJ/m^2 may also not be correct. The surface energy of Gr has a wide range of values depending on grade, contamination level, degree of orientation, and the plane of the Gr exposed at the surface [4].

The third assumption is the question of which interfacial surface energy is actually being measured. No allowance was made for the presence of a reaction layer at the interface such as that shown in Figure 4a. To account for the reaction layer the surface energy of the reaction layer should be used instead of the surface energy of Gr [7, 10]. This in turn requires knowledge of the interfacial reaction products and their surface energies. While the reaction products can be determined experimentally, in most cases their surface energies are not known.

SUMMARY

Sessile drop tests have been conducted on twelve Cu-based alloys to determine if the wetting of Gr by liquid Cu can be improved through alloying additions. Of the alloys studied, Fe, La, Mn, Nb, Si , Ta and Ti did not wet H-490 Gr at the alloying levels examined. The additions of Hf, Y and Zr decreased the wetting angles, but did not reduce the angles to much below 111° at the alloying levels investigated. The additions of Cr and V at approximately the level of 1 at% were able to enhance the wetting behavior such that wetting angles of 45°, or less, were produced. However, because of the difficulties of dissolving V in liquid Cu, a temperature of 1530°C was needed to achieve that degree of wetting.

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REFERENCES

[1] D. McDanels and J. Diaz, "Exploratory Feasibility Studies of Graphite Fiber Reinforced Copper Matrix Composites for Space Power Radiator Panels", NASA TM-102328 (1989).

[2] F. Weitzer, K. Remschnig, J. C. Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N," J. *Mat. Research*, 5 [10] 2152-59 (1990).

[3] B. Ash and S. Fowser, Personal communications.

[4] D. Mortimer and M. Nicholas, "The Wetting of Carbon by Copper and Copper Alloys", *J. Mat. Sci.*, 5 [2] 149-155 (1970).

[5] K. Nogi, Y. Osugi and K. Ogino, "A New Method of Wettability Measurement Utilizing a Small Sample and Its Application to Graphite or a-SiC and Liquid Cu-Cr Alloy Systems," *ISIJ*, 30 [1] 64-9 (1990).

[6] N. Kishkoparov, V. Chentsov, I. Frishberg and V. Pastukhov, "Wetting of Natural Graphite by Copper Alloys," *Sov. P. Met. and Met. Cer.*, [11] 869-70 (1984).

[7] M. Nicholas and D. Mortimer, "The Wetting of Carbon by Liquid Metals and Alloys"; pp. 1-3 in proceedings of International Conference on Carbon Fibers, their Composites and Applications, London, February 2-4, 1971.

[8] L. Murr, "Interfacial Free Energy"; p. 102 in Interfacial Phenomena in Metals and Alloys. Addison-Wesley Publ. Co., Reading, MA, 1974.

[9]W. Kingery, "Surface Energy"; p. 368 in Property Measurements at High Temperatures. Wiley and Sons, Inc., New York, 1959.

[10]R. Loehman, "Interfacial Reactions in Ceramic-Metal Systems," *Am. Ceram. Soc. Bull.*, **68** [4] 891-92 (1989).

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16. Abstract

Graphite surfaces are not wet by pure copper. This lack of wetting has been responsible for a debonding phenomenon that has been found in continuous graphite fiber/copper matrix composite materials subjected to elevated temperatures. By suitably alloying copper, its capability to wet graphite surfaces can be enhanced. In situ measurements of graphite/copper alloy wetting angles have been made using the sessile drop method. Interfacial energy values have been calculated based upon these measurements.

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