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REACTION LAYER FORMATION AT THE GRAPHITE/COPPER-CHROMIUM ALLOY INTERFACE

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ABSTRACT

Sessile drop tests were used to obtain information about copper-chromium alloys that suitably wet graphite. Characterizations of graphite/copper-chromium alloy interfaces subjected to elevated temperatures were conducted using scanning electron microscopy, energy dispersive spectroscopy, auger electron spectroscopy and x-ray diffraction analyses. These analyses indicate that during sessile drop tests conducted at 1130°C for 1 hour, copper alloys containing greater than 0.98 at% chromium form continuous reaction layers of approximately 10 μm thickness. The reaction layers adhere to the graphite surface. The copper wets the reaction layer to form a contact angle of 60° or less. X-ray diffraction results indicate that the reaction layer is chromium carbide. The kinetics of reaction layer formation were modelled in terms of bulk diffusion mechanisms. Reaction layer thickness is controlled initially by the diffusion of Cr out of the Cu alloy and later by the diffusion of C through chromium carbide.

I. INTRODUCTION

Continuous fiber reinforced graphite/copper (Gr/Cu) composites offer the 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 engine heat exchanger materials for hypersonic

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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 ceramic/metal interfaces is the ceramic/metal 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 metal and fibers. This intrinsic lack of wetting causes difficulties in production of the composites. More importantly, the lack of wetting can lead to fiber/matrix debonding and pore formation during the service life of the composites at elevated temperatures [1].

II. BACKGROUND

To date, limited work has been conducted in the area of Gr/Cu interfaces. Perhaps the most widely referenced studies have been those of Mortimer and Nicholas [3, 4, 5]. They reported that small additions of Cr reduce the contact angle formed by Cu on HX30 Gr and vitreous carbon in studies conducted in vacuum. Through metallographic examination, they found the presence of reaction products at the interfaces of the Gr/Cu-Cr alloy samples. Four types of reaction products were identified: continuous layers of uniform thickness, discontinuous layers of nearly uniform thickness, flaky layers partly detached from the carbon substrate and interfacial areas containing many small particles. The reaction product of the Cu-1at%Cr alloy was continuous, and quantitatively determined to be Cr_3C_2 .

For sessile drop experiments conducted under conditions where a continuous reaction layer forms, the appropriate form of the Young-Dupre equation [3] is as follows:

$$\gamma_{SV_{\text{carbide}}} = \gamma_{LV_{\text{alloy}}} \cos \theta_{\text{carbide/alloy}} + \gamma_{SL_{\text{carbide/alloy}}} \quad (1)$$

where $\gamma_{SV_{\text{carbide}}}$ is the carbide/vapor interfacial energy, $\gamma_{LV_{\text{alloy}}}$ is the alloy/vapor interfacial energy, $\theta_{\text{carbide/alloy}}$ is the contact angle between the carbide and the alloy and $\gamma_{SL_{\text{carbide/alloy}}}$ is the carbide/alloy interfacial energy. The values for $\gamma_{LV_{\text{alloy}}}$ for Cu-Cr alloys are not known, but are assumed to be less than or equal to that of the interfacial energy of pure Cu and its vapor, $\gamma_{LV_{\text{Cu}}}$. The value for $\gamma_{LV_{\text{Cu}}}$ has been determined as a function of temperature [6].

Mortimer and Nicholas [5] and Ramqvist [7] have conducted sessile drop tests of Cu on Cr₃C₂ substrates. Both investigations measured a contact angle of 45 to 50°. This contrasts with nonwetting angles of approximately 140° observed for pure Cu sessile drops on graphite substrates [3]. From their studies, Mortimer and Nicholas estimated the interfacial energy of Cr₃C₂ to its vapor to be 975 to 1070 mJ/m² [4, 5].

Nogi et al. [8] have conducted similar sessile drop experiments in an Ar-5H₂ atmosphere with Cu alloys on single crystal Gr substrates. They also concluded that Gr is wet by Cu-Cr alloys when the Cr content is high enough to create a continuous reaction layer at the interface.

In this study, sessile drop tests of Cu alloys containing a range of Cr contents on Gr substrates were investigated to determine their wetting behavior and extent of reaction layer formation. The nature of the reaction layers formed is then discussed in terms of thermodynamic and kinetic factors influencing reaction layer formation and its implication for actual Gr/Cu composites.

III. EXPERIMENTAL PROCEDURE

Extruded bar stock from vacuum induction melted Cu alloys containing 0.61, 0.98, 1.10 and 1.22 at%Cr was used for sessile drop evaluations. Tests were also run using pure OFHC

Cu as a standard. The chemical composition of each alloy was verified through ICP emission spectroscopy and atomic absorption spectrophotometry.

Sessile drop tests were conducted at 1 atmosphere pressure in argon gas of 99.995% minimum purity. 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-Cr alloy test specimen of 1.9 cm diameter and 2 mm height 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 $\leq 5^\circ\text{C}$. 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-Cr alloy and the Gr were simultaneously heated to the melting point of the alloy, approximately 1083°C . 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.

Sessile drop test specimens were cross-sectioned, mounted in epoxy and polished to a 0.25 μm diamond finish. The specimens were examined in the transverse direction using a JOEL 840-A scanning electron microscope (SEM). The continuity and thickness of the reaction layer of each sample were determined. Using a Kevex system with an ultra-thin window detector, energy dispersive spectroscopy (EDS) analyses were conducted. X-ray spectra of the bulk alloy, the reaction layer and bulk Gr were obtained. Additional analyses of cross sectional specimens were performed using a PHI 660 scanning auger microscope (SAM) system. Using a Philips APD 3500 diffractometer, an x-ray spectrum was obtained from the reaction layer of the Gr/Cu-0.61at%Cr sessile drop specimen in the normal to the surface

orientation to define which chromium carbide phase initially forms. An untested surface of a Gr substrate was also analyzed for calibration purposes.

IV. RESULTS

Sessile Drop Test

A value of 157° was observed for the contact angle of pure Cu on Gr. The contact angle measurements for the Cu-Cr alloys, along with the associated interfacial energy calculations based upon equation 1, are summarized in Table I. These data were obtained at a temperature of 1130°C . The values reported are for the equilibrium angle. Most alloys reached equilibrium within 100 s after melting. The interfacial energy calculations were made using values of 1279 mJ/m^2 [6] for $\gamma_{\text{LV}_{\text{alloy}}}$ and 975 mJ/m^2 for $\gamma_{\text{SV}_{\text{carbide}}}$ [3]. The value for Cu was assumed to be constant with alloying level. By increasing the amount of Cr addition, the contact angle of the Cu alloy on Gr can be reduced. The results correspond to those found by others [3, 4, 5, 7, 8].

Table I. Gr/Cu-Cr alloy sessile drop test results.

Cu-alloy at%Cr	Cu-alloy O, ppm	contact angle, $^\circ$	$\gamma_{\text{carbide/Cu}}$ mJ/m^2
0.61	66	114	1495
0.98	13	60	336
1.10	16	45	71
1.22	11	41	10

Scanning Electron Microscopy

Micrographs of each Cu-Cr alloy were obtained using the scanning electron microscope. This was done to establish the presence of a reaction layer at the interface, and to determine its thickness and continuity. Figures 1 and 2 contain micrographs of the interfaces formed from the sessile drop tests conducted with the Cu-0.61 and 1.22 at%Cr alloys. As indicated in Figure 1, the reaction layer formed at the Gr/Cu-0.61at%Cr alloy interface is discontinuous and approximately 1.3 μm thick. The Cu alloy sessile drop did not adhere to the reaction layer phase and is therefore not present in the micrograph. The interfaces formed with the higher Cr content alloys developed continuous reaction layers of approximately 10 μm thickness as represented in Figure 2. These Cu alloy sessile drops adhered to the reaction layer phases which formed.

Figure 3 examines the edge of the sessile drop and the growth of the reaction layer associated with the Cu-1.10at%Cr alloy. As indicated, the reaction layer extends along the surface of the Gr substrate approximately 100 μm beyond the perimeter of the sessile drop.

Stress induced cracking occurred between the sessile drop and the reaction layer during metallographic preparation of many of the test specimens which revealed that the reaction layer formed at the Gr/Cu-Cr interface is strongly adherent to the Gr. The separation of the Cu from the reaction layer at the interface of the Cu-1.22at%Cr sessile drop test specimen is shown in Figure 4. The micrographs clearly indicate the adherence of the reaction layer to the Gr substrate.

A summary of the information obtained during the SEM analyses is given in Table II. The table describes the continuity and thickness of the reaction layer, the contact angle measured via sessile drop testing and the adherence of the Cu-Cr alloy to the Gr substrate.

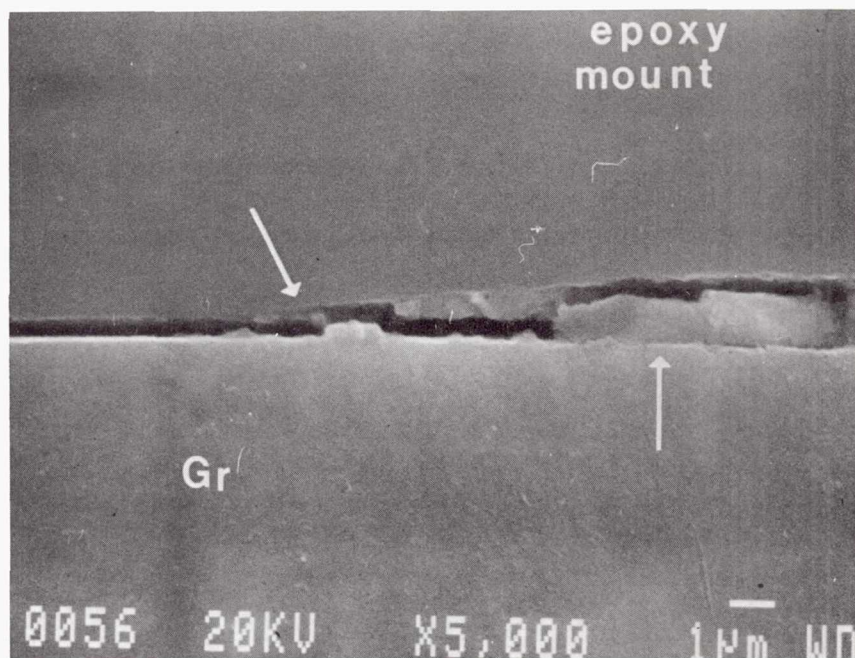


Figure 1. SEM micrograph of Cu-0.61at%Cr sessile drop specimen.
Discontinuous reaction layer on Gr substrate, 1.3 μm thick.

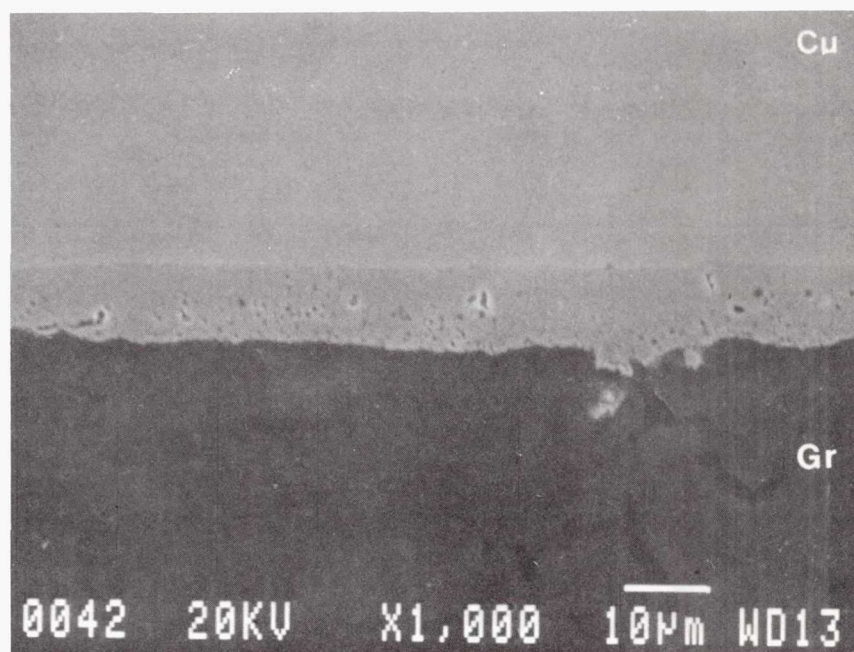


Figure 2. SEM micrograph of Cu-1.22at%Cr sessile drop specimen.
Continuous reaction layer, 10 μm thick.

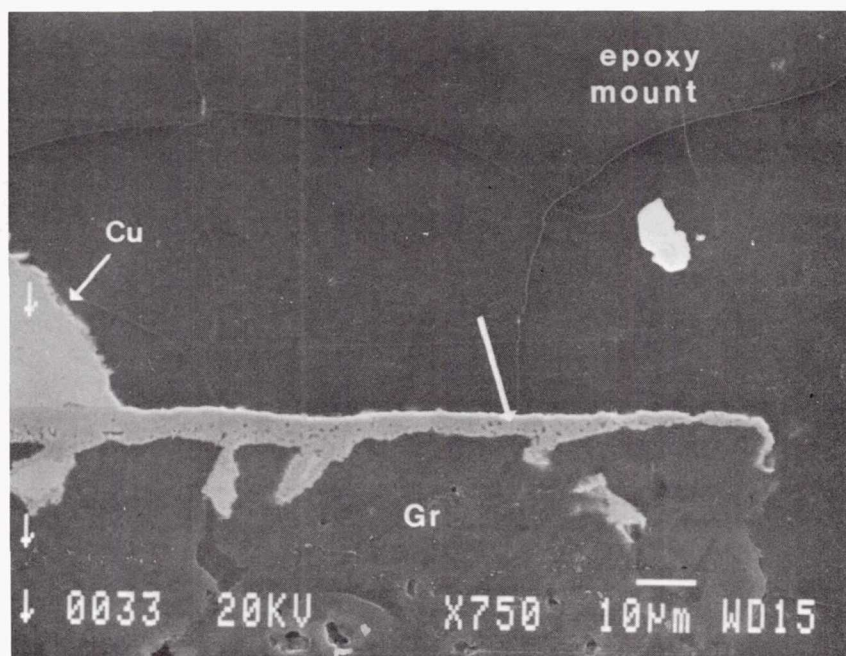


Figure 3. SEM micrograph of Cu-1.10at%Cr sessile drop specimen. Reaction layer extends radially along Gr surface approximately 100 μm .

Table II. Summary of scanning electron microscopy analysis of Cu-Cr alloys.

Cu-alloy at%Cr	description of layer	layer thickness, μm	contact angle, $^{\circ}$	Cu to Gr adherence
0.61	discontinuous	1.3	114	no
0.98	continuous	9	60	yes
1.10	continuous	8	45	yes
1.22	continuous	10	41	yes

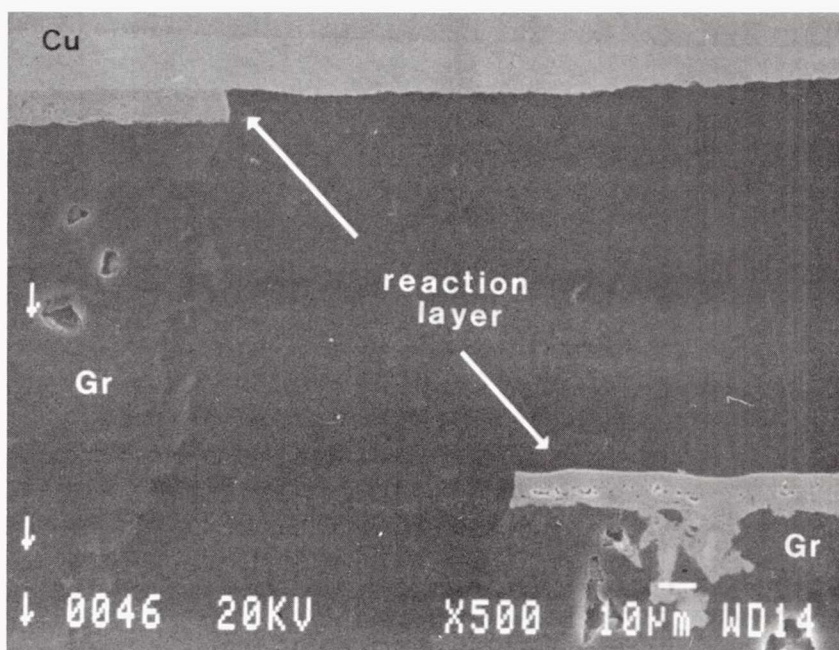
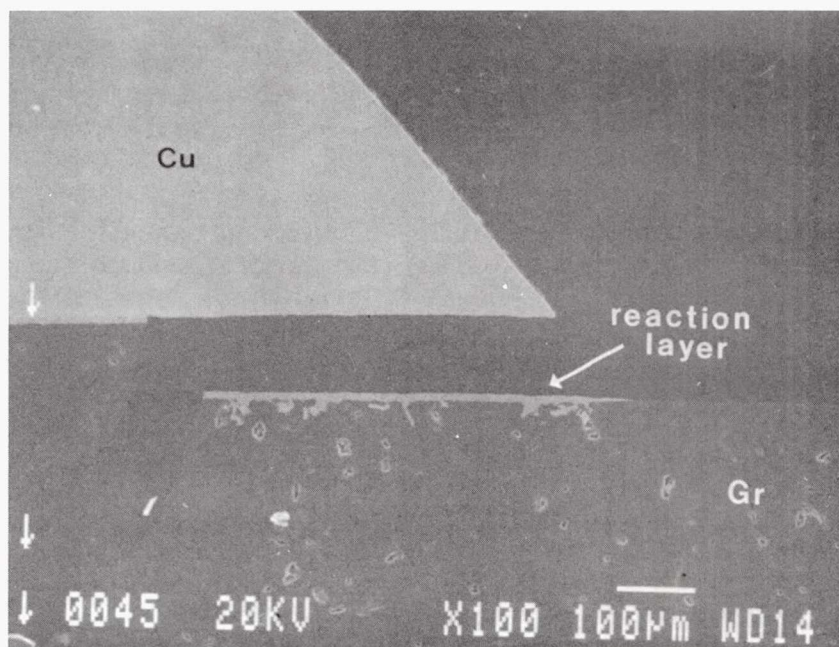


Figure 4. SEM micrograph of Cu-1.22at%Cr sessile drop specimen. Cu is separated from Gr at reaction layer. (a.) Low and (b.) higher magnification.

Energy Dispersive and Auger Electron Spectroscopy

The Cu-Cr alloy sessile drop test specimens were characterized using EDS and AES to qualitatively identify the chemical constituents comprising the reaction layer phase. The spectra for the Cu-1.22at%Cr sessile drop test specimen are included in Figure 5. The bulk alloy is shown to be comprised of Cu with a small amount of Cr. The reaction layer is shown to be primarily Cr with some C signal being indicated. The Gr bulk, as expected, shows only a very strong C peak. These results are representative of those found for the remaining Cu-Cr alloys. An AES line scan approximately 60 μm in length, starting in the Cu-Cr alloy crossing the reaction layer and extending into the Gr, is shown in Figure 6. There is a large increase in the Cr Auger peak-to-peak signal across the reaction layer. Figure 7 is an AES survey scan taken on the reaction layer after a 60 s sputter to remove all adventitious C. The high concentration of Cr and the presence of C is consistent with the reaction layer being a chromium carbide phase. The loss structure on the low energy side of the C peak also is consistent with the C being bound as a carbide phase.

X-Ray Diffraction

Because the chemical composition of the reaction layer could not be quantitatively determined with sufficient accuracy via EDS or AES analyses, to define which chromium carbide phase initially formed, x-ray diffractometry methods were employed. An x-ray diffraction scan was run on the reaction layer formed between the Cu-0.61at%Cr alloy and the Gr substrate. Although the reaction layer that remained adherent to the Gr substrate was discontinuous and had a maximum thickness of 1.3 μm , chromium carbide peaks of sufficient size and number were observed to make a unique identification. The peaks observed are listed in Table III where they are compared to those of the Cr_3C_2 phase [9]. Some of the Cr_3C_2 phase peaks were obscured due to the presence of much stronger Gr peaks generated by the substrate.

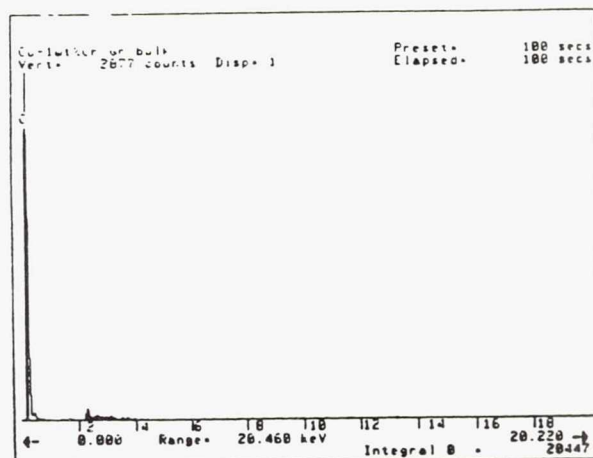
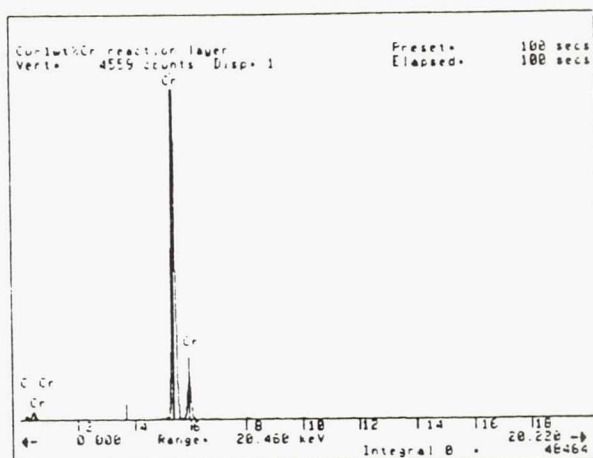
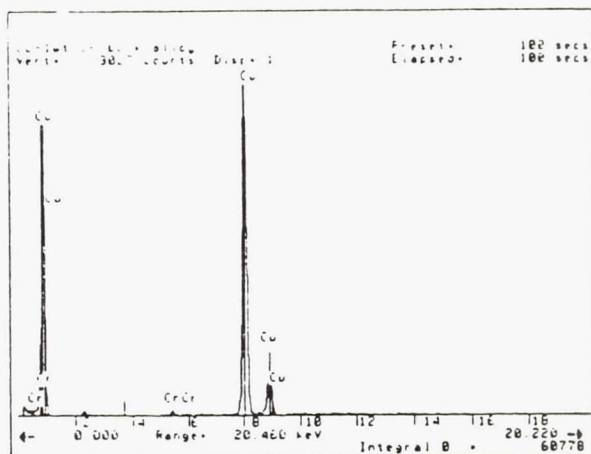


Figure 5. EDS spectra of Cu-1.22at%Cr sessile drop test specimen.
 (a.) Cu alloy bulk, (b.) reaction layer and (c.) Gr bulk.

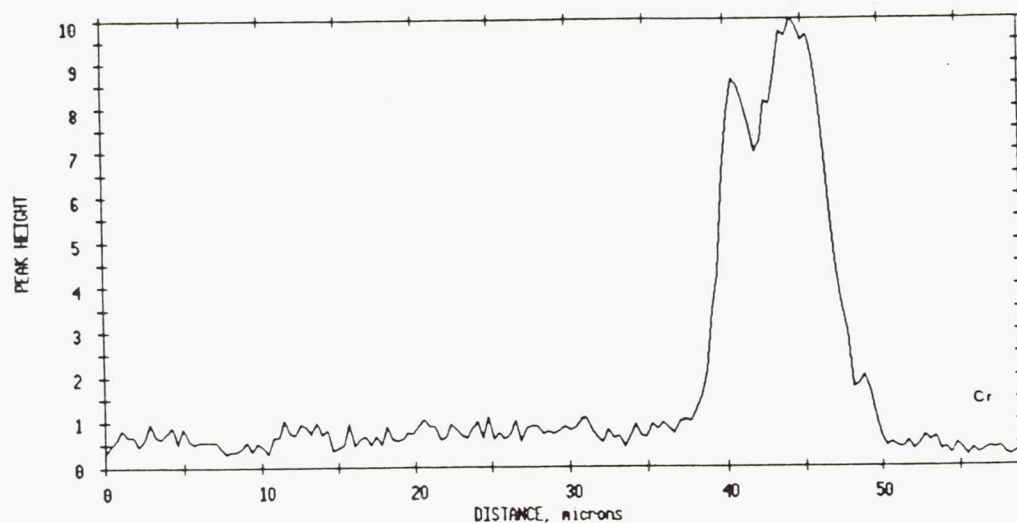


Figure 6. AES line scan of Cr over the interfacial region of a Cu-1.22at%Cr sessile drop specimen after 6 s sputter.

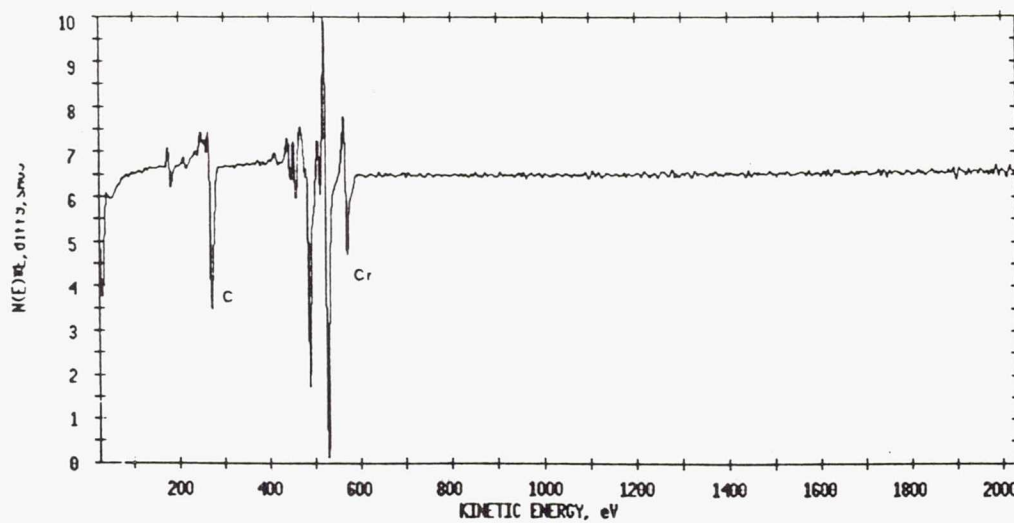


Figure 7. AES survey scan of Cu-1.22at%Cr reaction layer after 60 s sputter.

Table III. X-ray diffraction results from the reaction layer phase formed at the Gr/Cu-0.61at%Cr interface.

JCPDS 35-804 Cr ₃ C ₂	observed peaks	JCPDS 35-804 Cr ₃ C ₂	observed peaks
4.9780	†	1.7833	1.80
3.9830	†	1.7670	1.77
3.1460	†	1.7567	1.77
2.7460	†	1.6975	1.69
2.5478	2.55	1.6602	*
2.4897	2.49	1.6286	†
2.4596	2.45	1.5734	1.57
2.3063	2.32	1.5302	1.53
2.2751	2.27	1.4987	1.49
2.2409	2.25	1.4375	1.44
2.1215	*	1.4193	1.42
2.1036	*	1.4143	1.41
1.9912	1.99	1.3902	*
1.9482	1.94	1.3720	1.37
1.9151	1.92	1.3273	†
1.8934	*	1.2997	1.30
1.8691	1.87	1.2812	1.29
1.8190	1.82		

† not observed

* graphite interference

V. DISCUSSION

Thermodynamics of Cr_3C_2 formation

The degree of wetting of liquid Cu on the Gr substrate is shown to be affected by whether the carbide reaction layer is continuous or discontinuous as discussed by Nogi et al. [8]. Analyses of the Cu-Cr alloy interfaces, summarized in Table II, confirmed that the best wetting is obtained when a continuous reaction layer formed. It has also been noted that only when a continuous reaction layer is formed does the Cu alloy test specimen adhere to the Gr substrate.

To start a thermodynamic assessment of the most stable chromium carbide phase, the activity of Cr in the liquid Cu sessile drop was determined. As indicated by the x-ray diffraction results, the reaction layer phase that forms at the Gr/Cu-Cr alloy interface is Cr_3C_2 . This result is consistent with thermodynamic considerations of the most stable reaction layer phase. From the Cu-Cr phase diagram [10], at 1130°C the Cr liquid-solid transition occurs at $X_{\text{Cr}} = 0.02$, a composition of 2 at%. Assuming Henrian behavior, the activity coefficient of Cr in liquid Cu is found to be approximately 50. For the Cu-1.22at%Cr alloy used for the sessile drop experiments, the activity of Cr in liquid Cu is 0.61. Taking the activity of C in the graphite substrate as unity, and that the chromium carbide phases form as pure substances, the free energy of formation for each potentially stable carbide phase can be determined [11]. The results of these calculations, based upon a gram-atom of the carbide phase, are listed in Table IV. The Cr_3C_2 phase is observed to be the most stable. Using the same thermochemical data regarding the formation of Cr_3C_2 , the minimum Cr concentration in liquid Cu at 1130°C , at which Cr_3C_2 can form, was also calculated. The Cr level can be reduced to 0.078 at% before equilibrium is achieved.

Table IV. Free energies of formation of Cr-carbide phases at 1130°C.

Reaction	ΔG , cal/g-atom
$\frac{3}{5} \text{Cr} + \frac{2}{5} \text{C} = \frac{1}{5} \text{Cr}_3\text{C}_2$	-4594
$\frac{7}{10} \text{Cr} + \frac{3}{10} \text{C} = \frac{1}{10} \text{Cr}_7\text{C}_3$	-4065
$\frac{23}{29} \text{Cr} + \frac{6}{29} \text{C} = \frac{1}{29} \text{Cr}_{23}\text{C}_6$	-2741

Mass balance calculations verify the feasibility of forming a reaction layer of 10 μm thickness with the Cu-1.22at%Cr alloy. Using a radius of 9.5 mm and a thickness of 2.0 mm, the volume of the Cu-Cr sessile drop was calculated to be 570 mm^3 . The volume of a reaction layer of 10 μm thickness is 2.9 mm^3 . Using a density of 6.68 g/cm^3 for Cr_3C_2 , and assuming that the Cr level in the sessile drop can be reduced to 0.078at% before the formation of Cr_3C_2 becomes thermodynamically unfavorable, a potential carbide layer volume of 8.2 mm^3 can form from the Cu-1.22at%Cr alloy. Based on a mass balance analysis, a carbide layer approximately 2.8 times thicker than that observed could have formed.

Kinetics of Cr_3C_2 formation

The preceding discussion indicates that sufficient Cr was available in the liquid Cu sessile drops to form reaction layers consisting of Cr_3C_2 that were greater than 10 μm in thickness. The fact that layers thicker than 10 μm were not observed indicates that kinetic factors were influencing the reaction layer growth. Several possible mass transport mechanisms could be controlling the final thicknesses of the reaction layers that were observed.

The first kinetic factor to be explored is the rate of diffusion of Cr out of the liquid Cu. This process can be modelled using the simplified sessile drop geometry shown in Figure 8.

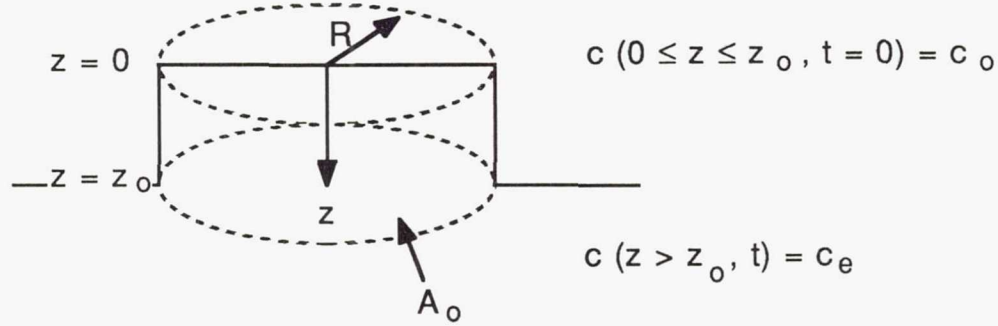


Figure 8. Simplified sessile drop geometry indicating boundary conditions for determining rate of diffusion of Cr out of liquid Cu.

The following equation defines the time dependent concentration of Cr in the cylindrical volume shown in Figure 8, assuming solute can only exit the volume through the bottom interface [12]:

$$c(z,t) = c_e + (c_0 - c_e) \sum_{n=1}^{\infty} \frac{2 \left(\frac{k}{D} \right) \cos \alpha_n z}{\left[\alpha_n^2 + \left(\frac{k}{D} \right)^2 \right] z_0 + \left(\frac{k}{D} \right)} \cos \alpha_n z_0 \exp(-D \alpha_n^2 t) \quad (2)$$

where c_e = concentration of Cr in equilibrium with Cr_3C_2 (0.078at%)
 c_0 = initial concentration of Cr in the sessile drop (1.22at%)
 D = diffusion coefficient of Cr in liquid Cu at 1130°C [13] ($3 \times 10^{-6} \text{ cm}^2/\text{s}$)
 k = interfacial mass transfer coefficient between the sessile drop and the Cr_3C_2 reaction layer
 t = time

and α_n is defined by the roots of the following transcendental equation [12]:

$$z_0 \alpha_n \tan z_0 \alpha_n = \left(\frac{k}{D} \right) z_0 \quad (3)$$

The total flux of Cr out of the bottom interface of the sessile drop, J, can be determined using the following equations:

$$J_{\text{total}} = \int_0^t -A_o D \frac{dc}{dz} \Big|_{z=z_o} dt \quad (4a)$$

$$J = A_o(c_o - c_e) \sum_{n=1}^{\infty} \frac{2 \left(\frac{k}{D} \right) \sin \alpha_n z_o}{\alpha_n \left[\alpha_n^2 + \left(\frac{k}{D} \right)^2 \right] z_o + \left(\frac{k}{D} \right)} \cos \alpha_n z_o [1 - \exp(-D \alpha_n^2 t)] \quad (4b)$$

The total flux of Cr that can exit through the bottom interface of the sessile drop of the Cu-1.22at%Cr alloy is plotted as a function of time in Figure 9 for several possible values of the interfacial mass transfer coefficient. The figure shows that for interfacial mass transfer coefficient values greater than 1.5×10^{-4} cm/s, interfacial transport is not greatly influencing the rate of Cr exiting the sessile drop. Under such conditions, more than half of the total available Cr level of 7.4×10^{-4} moles in the sessile drop could exit in 3600 s, the duration of the sessile drop tests conducted.

A second kinetic factor to be explored is the rate of C diffusion through the solid Cr_3C_2 layer at 1130°C. This process leads to a model for parabolic growth of the Cr_3C_2 layer. The following equation defines the thickness of the reaction layer, h, as a function of time, t [14]:

$$h = \sqrt{\frac{2(c_1 - c_2)Dt}{c_2}} \quad (5)$$

where c_1 = concentration of C in the Cr_3C_2 at the graphite interface
 c_2 = concentration of C in the Cr_3C_2 at the sessile drop interface
 D = diffusion coefficient for C in solid Cr_3C_2 at 1130°C [15]

The concentration variation for C across the Cr_3C_2 layer at 1130°C is known to be very small based upon the C-Cr phase diagram [16]. For sake of calculation a value for $(c_1 - c_2)/c_2$ of 0.01 was assumed. The diffusion coefficient for C in Cr_3C_2 is not known, but the activation

energy for the diffusion coefficient has been determined to be 45 kcal/mole [15]. Using equation 6 and a known reaction layer thickness of 10 μm in 3600 s, values of $D_0 = 0.14 \text{ cm}^2/\text{s}$ and $D = 1.3 \times 10^{-8} \text{ cm}^2/\text{s}$ at 1130°C were determined.

Using equation 5, the thickness of the Cr_3C_2 reaction layer was determined as a function of time and plotted in Figure 10. For comparison, the thickness of reaction layer that could be produced by the total flux of Cr out of the liquid Cu sessile drop, shown in Figure 9, is also plotted in Figure 10. In this latter case, a value for the interfacial mass transfer coefficient of $1.5 \times 10^{-3} \text{ cm/s}$ was used. Only for the first 100 s of growth, up to a reaction layer thickness of approximately 1.6 μm , is diffusion of Cr out of the sessile drop controlling the rate of growth of the reaction layer. From that point onward, diffusion of C through the Cr_3C_2 layer controls the rate of growth.

The other interesting observation regarding the Cr_3C_2 reaction layer was its extension beyond the edge of the sessile drop. As was shown in Figure 3, the layer extended radially outward on the order of 100 μm from the perimeter of the sessile drop. At 1130°C, the equilibrium vapor pressure of liquid Cu is 0.145 Pa [17]. At such a high vapor pressure the exchange of a monolayer of atoms between the liquid Cu surface and the vapor phase occurs in approximately 0.001 s. In the large bell jar chamber used for the sessile drop experiments the equilibrium vapor pressure of Cu was never established. So, evaporation of Cu was occurring throughout the experiments. The maximum evaporation rate possible would have been about 1000 atomic layers of Cu per second. At such an evaporation rate, considerably more than a 100 μm thick layer of Cu could have evaporated from the surface of the sessile drop during the typically 3600 s hold at temperature. Thus, as the evaporation of Cu continued during an experiment, an increasing amount of the chromium carbide reaction layer was exposed. This led to the observation shown in Figure 3 of the reaction layer extending out from under the sessile drop at the termination of a test.

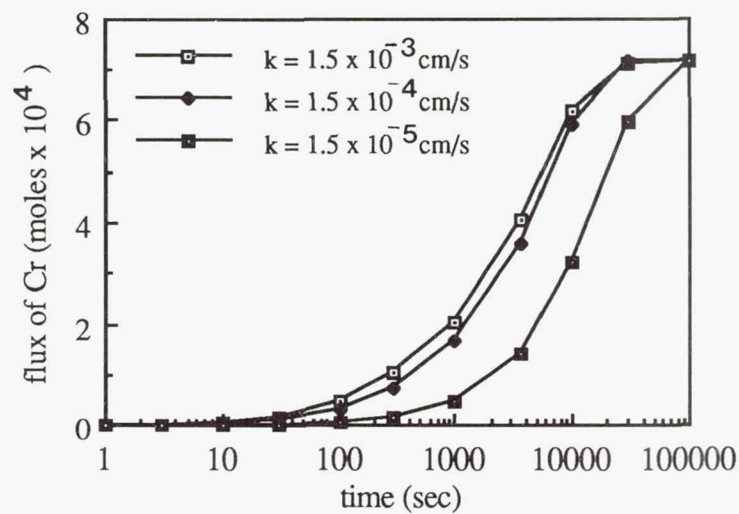


Figure 9. Flux of Cr out of liquid Cu sessile drop at 1130°C.
Flux through bottom surface, impermeable top and sides.

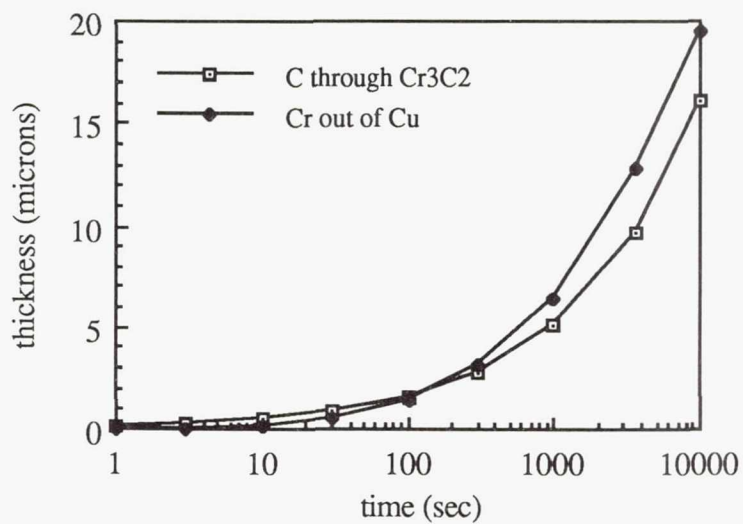


Figure 10. Reaction layer thickness as a function of time at 1130°C.
Controlling growth mechanisms: diffusion of Cr out of liquid Cu,
and diffusion of C through solid Cr₃C₂.

Implications for Gr/Cu composites

Many favorable properties of Gr fibers are attributed to their surface finish. Because of this, considerable concern has been noted of the possibility of severe degradation of Gr fibers from gross reaction layer formation [3, 4, 5]. Severe damage to the fiber surface could lead to degradation of the overall composite properties. Having observed reaction layers with thicknesses up to 10 μm for the sessile drop configuration, it is necessary to calculate the thickness of the reaction layer expected in an actual composite. The amount of the Gr fiber that will be consumed by the reaction can also be estimated.

The thickness of the Cr_3C_2 reaction layer that forms in actual Gr/Cu composites is much reduced compared with that which forms in the sessile drop tests because of the greatly increased Gr surface area per volume of Cu-Cr alloy. The following expression gives the Gr surface area per unit volume of composite, S_V :

$$S_V = \frac{2V_V}{r} \quad (6)$$

where V_V = volume fraction of Gr fibers in the composite
 r = radius of Gr fibers

For a volume fraction of 0.5, 5 μm radius Gr fibers, the Gr surface area/volume is 200 mm^2/mm^3 . For a Cu-1.22at%Cr alloy matrix there is only enough Cr available to form a Cr_3C_2 reaction layer 36 nm thick around the Gr fibers, assuming a homogeneous distribution of fibers. If a leaner alloy with 0.12at%Cr were used as the matrix, the maximum reaction layer thickness would be reduced to 1.5 nm.

The atomic volumes of C in Gr and Cr in Cu are approximately 8.8 and 12 \AA^3 , respectively [18]. This implies that a distance equal to about one third of the thickness of the Cr_3C_2 reaction layer formed would come from the surface of the Gr fibers; two thirds of its

thickness would come from the Cu-Cr alloy. Therefore, the formation of the reaction layer phase consumes only a limited percentage of the Gr fiber.

The molecular volume of Cr_3C_2 based upon a density of 6.68 g/cm^3 is approximately 44.7 \AA^3 . There is a reduction in volume of 16.5% when C in Gr and Cr in Cu combine to form Cr_3C_2 . If the reaction layer forms when the Cu-Cr alloy matrix is in the solid state, to maintain continuity the fibers and the reaction layer will be put into a state of residual tension [19]. The matrix will be put into a state of pure shear if it is assumed that no outside forces are exerted by one fiber upon another.

VI. CONCLUSIONS

All four Cu-Cr alloys with Cr contents of 0.61 to 1.22 at% formed reaction layers with the Gr substrates when held at 1130°C for 3600 s. The initial reaction layer formed was identified by combined EDS, AES and x-ray diffractometry analyses to be Cr_3C_2 for the Cu-0.61at%Cr alloy. The molten Cu-Cr alloy sessile drops were found to wet the chromium carbide reaction layer to a contact angle of $\approx 45^\circ$ once the layer became continuous.

A thermodynamic analysis of the formation of chromium carbide phases from Cr dissolved in liquid Cu and C in Gr showed that Cr_3C_2 was the most stable of the candidate phases. The Cr content of liquid Cu at 1130°C would have to be reduced to below 0.078at% before the formation of Cr_3C_2 would not be favorable. The formation of chromium carbide reaction layers about $10 \text{ }\mu\text{m}$ thick for the Cu-Cr alloys with approximately 1at%, or greater, Cr was found to be limited by diffusion through the carbide layer.

Because of the large Gr surface area to volume ratio in realistic Gr/Cu composite materials, the extent of reaction layer thickness should be limited to on average a few nanometers by the Cr content in the Cu alloy. The formation of a Cr_3C_2 reaction layer in the

solid state will put the Gr fibers and the reaction layer in a state of residual tension and Cu-Cr alloy matrix in a state of pure shear.

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