JOURNAL OF MATERIALS SCIENCE 5 (1970) 149-155

The Wetting of Carbon by Copper and Copper Alloys

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The effects of alloying additions on the wetting of two types of carbon, HX30 graphite and vitreous carbon, have been investigated, with a view to developing a system for metal impregnation of carbon fibre assemblies. Pure copper is inert and non-wetting but two additions caused the copper to wet: Cr on both substrates and V on the vitreous carbon only. Many of the additions formed a carbide reaction layer at the interface, and in the two wetting systems this was a thin, continuous, coherent layer. The data have been analysed in terms of the chemical and physical properties of the system and it was found that the wetting behaviour of copper alloys on HX30 graphite and vitreous carbon could be explained in terms of the behaviour of the reaction product carbides of the alloying addition when these existed.

1. Introduction

Carbon fibres have been successfully incorporated into resin matrices to give composites of high specific strengths. However, the nature of the matrix restricts the application of these composites to relatively low temperatures and hence there is considerable interest in the development of metal-matrix systems. One method of producing such composites is to infiltrate bundles of fibres with liquid metal. This technique has the advantages of, first, not subjecting the fibres to the rough handling associated with powder metallurgy operations which often degrade the fibres and, second, allowing high fibre packing densities to be attained.

If this infiltration is to be successful, the liquid metal/carbon fibre contact angle must be less than 90° and the fibres must not be degraded by extensive chemical reaction with the liquid metal. No pure metals are known that satisfy both criteria; those such as iron and nickel which wet carbon also seriously degrade it, and inert metals such as copper and tin [1] do not wet carbon. Aluminium is interesting in that it is inert and non-wetting at low temperatures, and chemically reactive and wetting on carbon at high temperatures [2]. A possible solution to the selection of an inert, wetting metal might be found by alloying in order either to improve the wetting by an otherwise inert metal, or to prevent the degradation of the carbon fibres by a wetting but reactive metal. In the present study the former approach was used with copper as the inert base metal.

This approach has been adopted by a few other workers. Takamori and Akanuma [3] investigated the brazing of pyrolytic graphite and recommended copper alloys containing 25 to 68% chromium as being particularly suitable. Naidich and Kolesnichenko [4] studied the wetting behaviour of copper alloys on diamond and, in some cases, graphite substrates. They showed that the addition of chromium or massive amounts of titanium, manganese or vanadium promoted wetting.

In view of the relative scarcity of data it was felt that a systematic surveying programme was justified. In this programme the wetting behaviour on carbon plaques of copper alloyed with 1 at. % of twenty different additions was investigated by measurement of sessile drop contact angles. There was some uncertainty as to which form of bulk carbon most resembled carbon fibres in surface properties, especially as several types of fibre are available. Carbon fibres have a graphite lattice and, like bulk graphite, are polycrystalline. The crystallite size of bulk graphite is about 1000 Å, but that of a carbon fibre is only 50 to 100 Å [5]. In view of these differences it was decided to use two forms of graphitic carbon in the surveying programme:

HX30 which is a typical bulk graphite, and vitreous carbon which is a new form of graphite with a crystallite size of only 15 to 25 Å [6]. It was hoped that differences in the wetting behaviour of alloys on these two substrates would be more extreme than those between differently produced carbon fibres.

2. Experimental Materials and Techniques

The substrate plaques, of either HX30 graphite or vitreous carbon, were 1 cm in diameter and 2 mm thick. These two forms of carbon have similar ash contents (50 to 250 ppm for HX30 graphite and ~200 ppm for vitreous carbon) and impurity levels. The principal physical property differences between conventional graphite and vitreous carbon are that vitreous carbon has a slightly lower density and interlamellar lattice spacing and a smaller crystallite size [6].

The metals employed were all spectroscopically pure. Alloys of copper with aluminium, chromium, molybdenum, niobium, tantalum, titanium, tungsten, uranium, vanadium and zirconium were used with both vitreous carbon and HX30 graphite substrates. In addition to these, other alloys of copper with boron, calcium, cobalt, hafnium, iron, manganese, nickel, platinum, rhenium and scandium were used with vitreous carbon substrates only.

The alloys were prepared *in situ* by machining a cylinder of copper, 3 mm in diameter and 5 to 6 mm high, with a hole in the top into which was placed the required amount of alloying addition, giving 0.3 g of 1 at. % alloy. The weighed metals were ultrasonically cleaned in methylated spirits for 5 min, then dried in a blast of hot air. The vitreous carbon substrates were ground on SiC papers and then polished with diamond paste to a $\frac{1}{4}$ μm finish. Because of porosity it was found that this process led to pull-out of large pieces of HX30 graphite. The graphite plaques, therefore, were polished on a 200 grit SiC paper and then on a dry Hyprocel pad. Examination with a Baker-Watson interference microscope showed that the two finishes were comparable. After polishing, the vitreous carbon plaques were cleaned in the same way as the metals but the graphite plaques were put straight into the furnace. The metal cylinder was placed on top of the plaque on a platform in a vacuum furnace heated by a tantalum split-cylinder element [7]. The furnace was pumped to below 1×10^{-5} torr* and the temperature raised slowly to 1050° C, keeping the pressure below 5×10^{-5} torr, to outgas the specimen. The temperature was then raised rapidly to 1145 ± 5° C and approximately 40 photographs of the sessile drop outline taken at regular intervals over a period of 2 h using a 35 mm camera. The contact angles were measured from an enlarged projected image of the photograph.

The solidified specimens were mounted in perspex, sectioned perpendicular to the interface, polished to $\frac{1}{4}$ μm diamond paste finish, and the interfacial regions examined optically and with a Geoscan electron microprobe analyser.

3. Results

Fig. 1 shows graphs of the measured contact angles of copper and several alloys on both HX30 graphite and vitreous carbon, plotted as a function of time at temperature, zero time being taken to be when the metal cylinder melted. Pure copper did not wet either substrate although the contract angles decreased slowly with time, possibly due to evaporation. The contact angles of most of the alloys did not differ by more than 25° from those of pure copper and, like those of pure copper, decreased slowly with time. The only additions that produced initially rapid changes of contact angle with time were vanadium with vitreous carbon substrates, and chromium with both HX30 graphite and vitreous carbon substrates. These alloy/substrate combinations were also the only ones which had contact angles of less than 90°. After 60 min at temperature, the contact angles of all the alloys were decreasing only very slowly, and therefore these 60 min contact angle data were selected for presentation in table 1 which summarises the wetting behaviour of all the alloy/substrate combinations.

Metallographic examination revealed the presence of reaction products at the interfaces of samples to which carbide-forming alloying additions had been made. There were four types of reaction product morphology which have been designated A, B, C and D: A – layers of near uniform thickness that extended all the way across the interfaces, B – layers of near uniform thickness that were present only at some parts of the interface, C – flakey layers that were partly detached from the carbon substrate, D – inter-

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*1 torr = 133.322 N m^{-2}

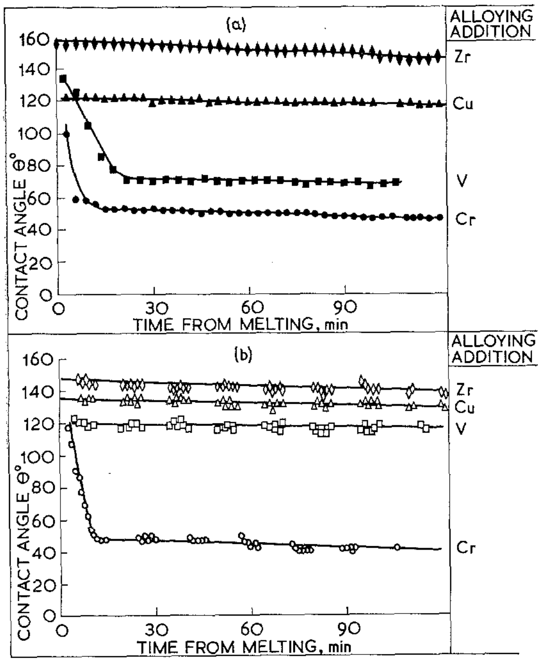

Figure 1 Contact angle versus time curves for copper alloys on (a) vitreous carbon and (b) HX30 graphite.

facial zones containing many small particles. Examples of all four types are shown in fig. 2. In the case of most samples having type B reaction products, there had been a separation between the alloy drop and the carbon substrate, so type B interfaces may be merely a modified form of type A. The metallographic evidence about the morphology of the reaction products is summarised in table I; the symbol 0 signifies that no reaction product could be seen.

The qualitative Geoscan electron microprobe analyser scans correlated with the interfacial morphology revealed by the metallography. Systems which formed continuous layers of reaction product showed sharp, smooth peaks in the concentration of alloying addition at the interfaces, systems which formed flakey or particulate reaction products showed sharp and ragged concentration peaks at the interfaces, and systems for which no reaction product was observed metallographically showed no concentration peaks at the interfaces. Some of the qualitative scans are presented in fig. 3. In addition to these qualitative analyses, the reaction product of the chromium alloy was analysed quantitatively. 84.3 wt % chromium was found, which suggests that the carbide was Cr_3C_2, which should contain 86.7 wt % of chromium. The other reaction product layers were too thin to allow quantitative analysis.

TABLE I Summary of wetting and compatibility data.

Alloying addition	Vitreous carbon substrates contact angle after 60 min, degrees	 reaction product type	HX30 graphite substrates contact angle after 60 min, degrees	 reaction product type
B	159	0	—	—
Al	—	—	127	0
Ca	111	B	—	—
Sc	147	B	—	—
Ti	135	B	128	A
V	68	A	117	C
Cr	50	A	45	A
Mn	139	B	—	—
Fe	149	O	—	—
Co	140	O	—	—
Ni	132	O	—	—
Zr	152	D	143	D
Nb	152	C	136	C
Mo	131	B	123	B
Hf	130	D	—	—
Ta	143	C	116	C
W	134	C	116	B
Re	138	P	—	—
Pt	135	O	—	—
U	118	A	128	A

4. Discussion

The experimental programme was performed in an attempt to identify alloying additions which

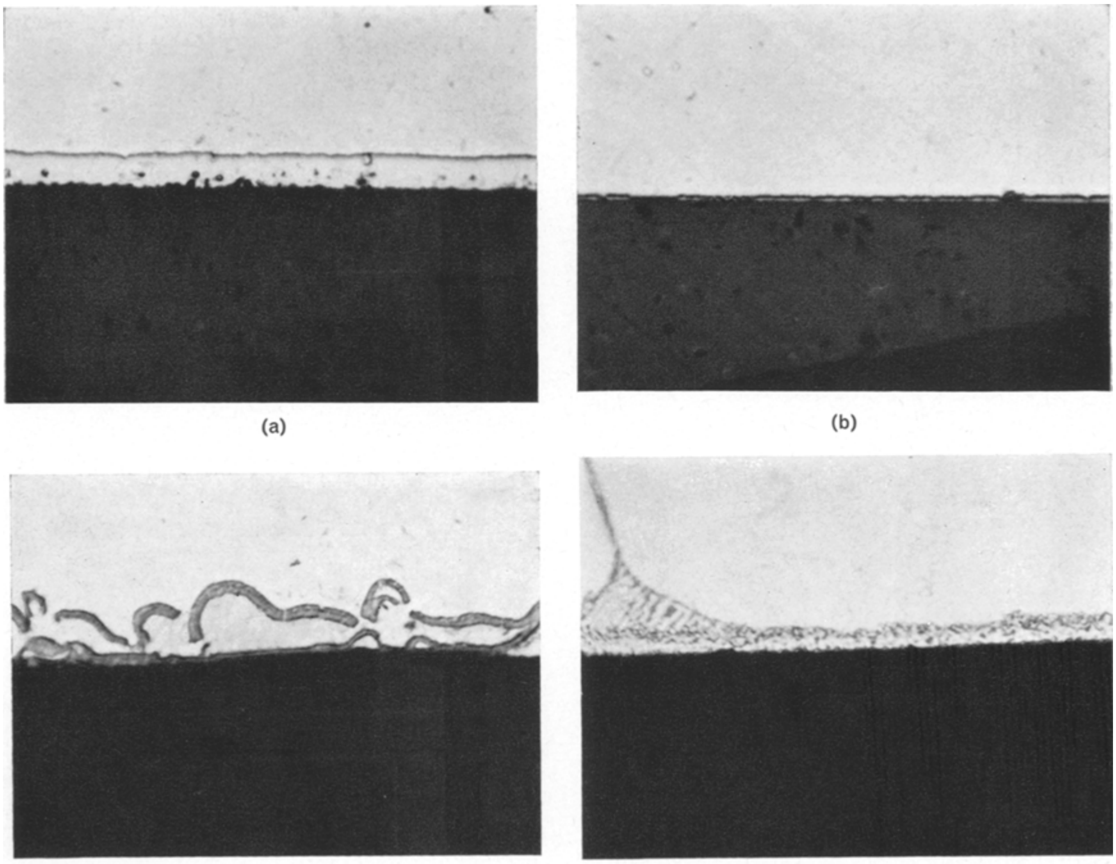
(a) (b) (c) (d)

Figure 2 Micrographs illustrating the various types of reaction product morphology observed. (a) 1% Cr alloy; (b) 1% Ti alloy; (c) 1% Ta alloy; (d) 1% Zr alloy (×600).

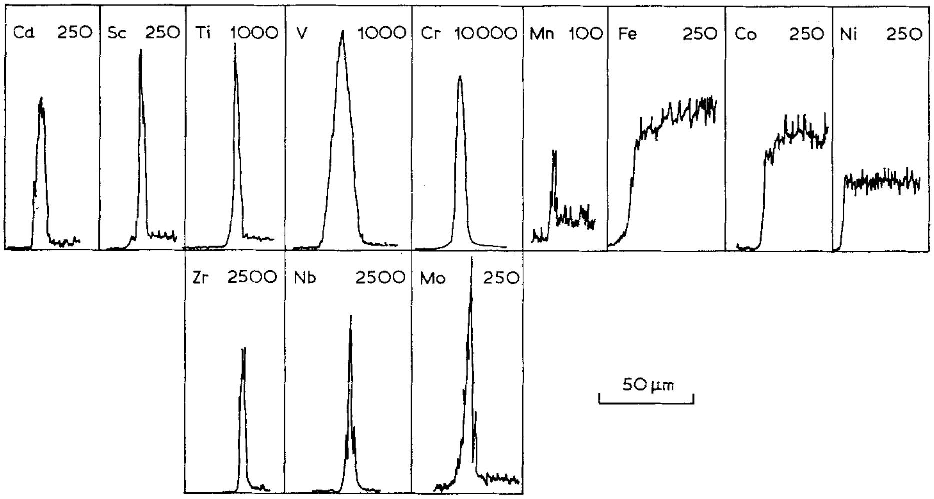

Figure 3 Geoscan EPMA traces across the interfaces of some vitreous carbon/copper alloy systems. Alloying element and count rates in counts/sec corresponding to box heights are indicated in the boxes.

would promote the wetting of carbon by copper without causing deleterious chemical reactions to occur at the carbon/metal interface. A secondary objective of the programme was to gain insight into the factors that control the wetting of carbon by liquid metals. Both of these objectives have been attained to some extent.

Two wetting systems have been identified. An addition of 1 at. % of chromium caused copper to wet both vitreous carbon and, confirming the Russian work, HX30 graphite. This alloy formed a thin, continuous and adherent layer of chromium carbide at the carbon/metal interface. Similarly an addition of 1 at. % of vanadium caused copper to wet vitreous carbon, but not HX30 graphite. The alloy formed a continuous adherent type A reaction layer on vitreous carbon but a flakey type C layer on HX30 graphite. Clearly the interaction of this alloy with carbon substrates is sensitive to the specific nature of the substrate and hence its behaviour may be variable with different types of carbon fibres. This alloy, however, is exceptional and there is little evidence to suggest that minor variations in the production processes of carbon fibre bundles will, in general, have marked effects on the ease with which they can be infiltrated by liquid metals.

The great majority of the alloying additions evaluated did not result in wetting. This was not unexpected because graphitic carbon is a solid with a low surface energy and, therefore, the metal/carbon interfacial energy would also have to be low for wetting to occur. This is inherently unlikely in view of the different lattice bonding mechanisms operative in carbon and in metals. However, a large body of wetting data was obtained during the experimental programme and this has been analysed in an attempt to define the factors that control wetting behaviour. Any such definition would be useful for example, in further studies in which some base metal other than copper is used.

The experimental data for both HX30 graphite and vitreous carbon substrates, taken as a whole, display evidence of periodicity in both contact angle values and reaction product morphologies. Alloying additions taken from groups IVA, VA and VIA of the periodic table tend to have the most significant effects on the contact angles of the copper alloys on both vitreous carbon and graphite substrates, the most beneficial effects being caused by additions from the 4th period. Not all the alloying additions formed visible reaction products, and therefore the data available for analysis in terms of reaction product morphology are somewhat restricted. The most desirable form of reaction product is a coherent and adherent layer and this is achieved most often by alloys containing additions chosen from the 4th period.

The description of wetting behaviour and reaction product morphology in terms of period and group number is merely a qualitative rationalisation of the experimental data. In an attempt to quantify the description, the contact angle data were analysed in terms of both the chemical and physical properties of the systems. It has been suggested frequently that there is a link between the wetting behaviour of alloys and the chemical reactivity of the active constituent [8–10]. However, this suggestion seems inapplicable to the wetting behaviour of carbon because there was no correlation between the alloy/carbon contact angles on either HX30 graphite or vitreous carbon substrates, and the free energies of formation of the most stable possible reaction product carbides as defined by Smithells [11].

Analysis of wetting behaviour in terms of physical properties, specifically the surface and interfacial tensions, was restricted to alloys that formed carbide reaction products and involved the assumption that the metal/substrate interfacial energy, γ_I, was identical for alloy/carbon and appropriate alloy/carbide systems, as illustrated in fig. 4. This assumption implies that a layer of the reaction product is present on the surface of the carbon substrate when in contact with any of the carbide-forming alloys, even those that formed particulate reaction products on the microscopic scale. Clearly this assumption is arbitrary but it is not thought to be unreasonable. If it is made, the Young equation for an alloy (M + X) on a carbon substrate can be written

$$\gamma_{SV_C} = \gamma_{LV_{M+X}} \cos \theta_{M+X/C} + \gamma_I , \qquad (1)$$

where γ_{SV_C} is the surface energy of carbon, $\gamma_{LV_{M+X}}$ is the surface energy of the liquid alloy and $\theta_{M+X/C}$ the contact angle of the alloy drop. If the carbon substrate is replaced by one of XC, the reaction product carbide, the Young equation may be written:

$$\gamma_{SV_{XC}} = \gamma_{LV_{M+X}} \cos \theta_{M+X/XC} + \gamma_I . \qquad (2)$$

Subtraction of equation 2 from 1 and rearranging yields

$$\gamma_{SV_{XC}} = \gamma_{LV_{M+X}} [\cos \theta_{M+X/XC} - \cos \theta_{M+X/C}] + \gamma_{SV_C} . \qquad (3)$$

In essence this analysis provides a description of the wetting behaviour of an alloy on carbon and on the appropriate reaction product carbide in terms of the surface energies of carbon and of the carbide. If the analysis is correct, a graph of $\gamma_{SV_{XC}}$ plotted against $[\cos\theta_{M+X/XC} - \cos\theta_{M+X/C}]$ should be linear, with a slope equal to $\gamma_{LV_{M+X}}$ and should intercept the $\gamma_{SV_{XC}}$ axis at γ_{SV_C}.

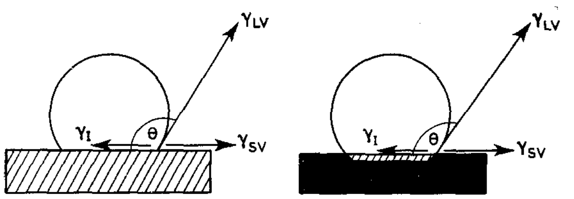

Figure 4 Schematic illustration of model for relating the wetting of carbon by carbide-forming alloys to that of the reaction-product carbide. Left: $\gamma_{SV_{xc}} = \gamma_{LV_{m+x}} \cos \theta_{m+x/xc} + \gamma_I$. Right: $\gamma_{SV_c} = \gamma_{LV_{m+x}} \cos \theta_{m+x/c} + \gamma_I$.

In order to test these predictions, values are needed for the two sets of contact angles and the carbide surface energies. Owing to the limited availability of such data two additional assumptions were made for the dilute alloys employed. These were:

(i) $\theta_{M+X/XC} = \theta_{M/XC}$;

(ii) $\gamma_{LV_{M+X}} = \gamma_{LV_M}$.

The first of these is convenient but arbitrary. The second should be valid provided the alloying additions have higher surface tensions than M, in this case copper, and do not form oxide films on the molten sessile drops in the experimental environments. With these additional assumptions, values of the bracketed term in equation 3 were calculated for eight copper alloy systems using the experimental values of $\cos\theta_{M+X/C}$ obtained in the present study for both vitreous carbon and HX30 graphite substrates, and the literature values of $\cos\theta_{M/XC}$ presented in table II. Also in table II are values of $\gamma_{SV_{XC}}$ taken from the literature. These are plotted in fig. 5 against the values calculated for the bracketed term.

Although the points on the graph are somewhat scattered, they are consistent with a linear relationship. As there does not seem to be any significant displacement of the HX30 graphite data from the vitreous carbon data, both sets were used in the statistical determination of the best straight line through the points. This line, which is drawn in fig. 5, has a slope of 1223 erg cm^{-2}, which is remarkably close to the surface tension of pure copper just above its melting point, 1239 erg cm^{-2} [18], and intercepts the ordinate axis at 798 erg cm^{-2}. According to equation 3, this intercept is equal to the surface energy of carbon, and in fact is of the same order of magnitude as the values reported in the literature for graphitic carbon, 119 to 1750 erg cm^{-2} [19–21].

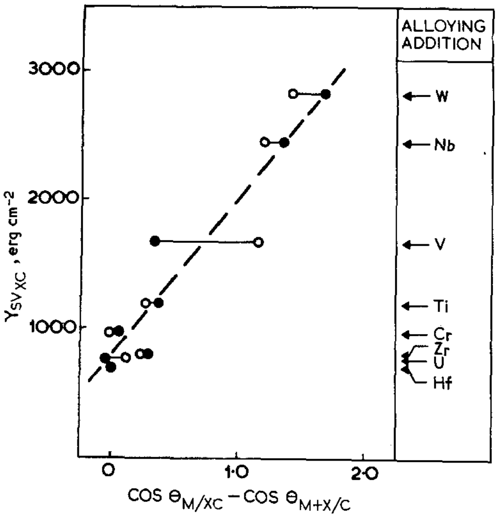

Figure 5 Plot of the parameters in equation 3. Full circles refer to vitreous carbon data, open circles to HX30 graphite data.

The experimental data for the copper-tantalum alloy were not plotted in fig. 5 because of the extreme uncertainty about the value of the surface tension of TaC. Livey and Murray [13] proposed a value of 1290 erg cm^{-2} but the present authors recently obtained a value [15] of 2690 erg cm^{-2} from an unduplicated experiment and a value of approximately 1800 erg cm^{-2} has been suggested [17] for somewhat impure TaC.

The experimental results for the wetting of carbon by copper alloys, therefore, can be interpreted in terms of the physical properties of the reaction product carbides and carbide/metal interfaces. Many carbide physical properties display variations with group and period number and this may account for the variations noted in the carbon wetting behaviour and reaction product morphology. This analysis has been tested only for copper alloys but it may be applicable to other alloyed metals provided the base metal is inert with respect to carbon, when the main problem is to improve wettability. Information on the wetting of carbides by metals that are chemically inert with respect to carbon, such as

TABLE II Carbide property data used in calculating values plotted in fig. 5.

Carbide XC	Contact angle, $\theta_{Cu/xc}$ degrees	Surface energy, γ_{SVxc} erg cm^{-2}
Cr_3C_2	46.5 (E)	975 (A)
HfC	132 (E)	690 (D)
NbC	62 (E)	2440 (A)
TiC	110 (E)	1190 (B)
UC	122 (F)	780 (C)
VC	46 (E)	1675 (B)
WC	14 (E)	2830 (A)
ZrC	126 (E)	800 (B)

A, Estimated value for 1150° C, [15].
B, Indirectly derived value for 1100° C, [13].
C, Extrapolation to 1150° C of experimentally determined values, [14].
D, Estimated value for 1150° C, [17].
E, Equilibrium value at 1150° C, [12].
F, Equilibrium value at 1150° C, [16].

gallium, lead, silver and tin, may be of considerable assistance in the selection of alloys to be used in the production of carbon fibre composites by the infiltration technique.

The essential condition for any alloying addition, X, to promote the wetting of carbon by an inert metal, M, is that the interfacial energy between M and XC should be less than the surface energy of carbon. Contact angle data for metal/carbide systems are not direct measures of interfacial energies and, therefore, care must be taken in their interpretation. This can be illustrated by considering the effects of chromium and tungsten on the wetting of carbon by copper. Copper wets WC better than Cr_3C_2, but the surface energy of WC is so large that good wetting occurs despite an interfacial energy of 1630 erg cm^{-2} [12, 15, 18]. On the other hand, Cr_3C_2 has a relatively small surface energy and the fact that copper wets it at all is an indication that the Cu/Cr_3C_2 system has a small interfacial energy – a value of 130 erg cm^{-2} can be calculated from the data in table II [12, 15, 18]. Thus, if the model described in this paper is valid, the interfacial energy between carbon and copper alloyed with tungsten will be much larger than the surface energy of carbon, and wetting will not occur; but the interfacial energy between carbon and copper alloyed with chromium will be smaller than the surface energy of carbon, and wetting will occur.

Acknowledgement

The authors wish to express their indebtedness to Mr J. E. Cope, a sandwich course student from the Physics Department of Portsmouth College of Technology, who made a substantial contribution to the experimental programme. It is also a pleasure to acknowledge the many fruitful discussions held with Dr D. M. Poole, the leader of the Physical Metallurgy Group of which the authors were members when the work was conducted. Finally, thanks are due to Miss Y. Wakeling who performed the Geoscan EPMA work.

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Received 13 October and accepted 29 October 1969.