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The wetting of carbon and carbides by copper alloys

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In a previous paper (*J. Mater. Sci.* **5** (1970) 149) a model was developed to predict the wetting behaviour between carbon and copper alloys containing 1 at.% of a carbide-forming element. In the present paper it is shown that the model can be applied successfully to alloys containing as little as 0.15 at.% chromium or vanadium and as much as 13 at.% titanium. A further development of the model is its use to predict carbide surface energies, the values derived being in good agreement with literature data.

1. Introduction

In an earlier paper, the wetting behaviour between carbon and copper alloyed with 1 at.% of various carbide formers was described [1]. The formation of carbide layers at the alloy/carbon interfaces enabled a model to be developed relating the wetting behaviour of alloys on carbon and carbide substrates. This model is illustrated in Fig. 1 which shows sessile drops of (Cu + X) resting on (i) a plaque of XC and (ii) a raft of XC produced by reaction with a carbon plaque. The Young's equations relating to the forces at the drop peripheries can be written as

$$\gamma'_{XC} = \gamma_{(Cu+X)} \cos\theta_{(Cu+X)/XC} + \gamma_{(Cu+X)/XC} \quad (1)$$

$$\gamma'_{C} = \gamma_{(Cu+X)} \cos\theta_{(Cu+X)/C} + \gamma_{(Cu+X)/C} \quad (2)$$

where γ'_{XC} and γ'_{C} are the surface energies of the carbide and carbon plaques in the presence of vapour distilled from the sessile drop; $\gamma_{(Cu+X)}$ is the surface energy of the sessile drop, $\gamma_{(Cu+X)/XC}$ and $\gamma_{(Cu+X)/C}$ are the drop/carbide and drop/carbon interfacial energies; $\theta_{(Cu+X)/XC}$ and $\theta_{(Cu+X)/C}$ are the corresponding contact angles. It was assumed that $\gamma_{(Cu+X)/XC}$ and $\gamma_{(Cu+X)/C}$ could be equated and hence that

$$\gamma'_{XC} - \gamma'_{C} = \gamma_{(Cu+X)} [\cos\theta_{(Cu+X)/XC} - \cos\theta_{(Cu+X)/C}]. \quad (3)$$

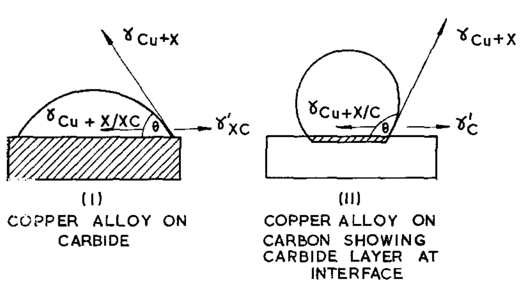

Figure 1 Schematic illustration of model relating the wetting of carbon by reactive copper alloys to that of the reaction product carbide.

In attempting to test the model, certain approximations had to be made because of the lack of relevant data. The most arbitrary of these was the use of $\theta_{Cu/XC}$ rather than $\theta_{(Cu+X)/XC}$ values. Nevertheless, the model satisfactorily described the behaviour of a wide range of 1 at.% alloys. For example, it correctly predicted that the addition of chromium would induce copper to wet and that the addition of titanium would make it even more non-wetting towards carbon.

The present paper describes work further developing the model and in particular establishing whether its applicability is limited to 1 at.% alloys and carbon substrates. The 1 at.% level was used in the early work merely because it was experimentally convenient and not because it related to solubility limits. Thus it is unlikely that vanadium or tungsten was dissolved in the copper [2, 3]. This suggests that 1 at.% of alloying addition is not necessary for the model to operate, but there must be a lower concentration, perhaps only a few parts per million, at

TABLE I Carbide analyses

Material	Composition (wt %)								
	C	Cr	Fe	N	O	Ti	Zr	C (free)	
Cr_2C_2	13.2	Rem	0.1	0.2	0.01	—	—	—	—
HfC	6.3	0.3	—	0.1	0.06	—	0.3	0.2	Hf rem
NbC	11.4	—	—	0.26	0.01	0.03	—	0.4	Nb rem
TiC	19.8	—	—	0.1	0.02	Rem	—	0.29	—
UC	4.67	—	—	0.024	0.028	—	—	—	U rem
VC	18.6	—	0.15	0.009	0.004	—	—	0.6	V rem
WC	6.1	—	—	0.015	0.002	—	—	0.03	W rem
ZrC	11.0	—	0.1	0.27	0.015	—	Rem	0.3	—

which it is inapplicable because there is insufficient alloying element present to create a continuous carbide layer at the alloy/carbon interface. At least in the case of titanium alloys, there is also an apparent upper concentration limit because the model fails to predict that massive additions of titanium will induce copper to wet carbon [4, 5]. This paper presents information about the minimum concentrations of chromium and vanadium needed to induce wetting, and the reasons why massive additions of titanium induce copper to wet carbon are discussed.

A second possible development of the model is to use Equation 3 to determine relative surface energies. Relevant contact angle data are presented in this paper and used to derive surface energy values for various carbides. The validity of this approach is then tested by comparing these derived values with published data.

2. Experimental materials and techniques

Two types of carbon substrates were employed, vitreous carbon and HX30 graphite. Both have graphitic lattice structures, and the ash contents and impurity levels are similar, but vitreous carbon has a slightly smaller interlamellar spacing and a much smaller crystallite size [6]. The vitreous carbon used was in the form of cylindrical plaques, 10 mm in diameter and 2 mm thick, the surfaces of which were polished to a 0.25 µm finish using diamond paste. The HX30 graphite substrates were 10 to 15 mm square plaques 2 to 3 mm thick. The surfaces of these plaques were polished on 200 grit SiC paper and dry Hyprocel pads to produce a finish comparable to that of the vitreous carbon samples.

The carbides used in the programme were in the form of discs, about 10 mm in diameter and 2 mm thick, which were sliced from ingots prepared at AERE. The UC ingots were arc melted but all the other carbides were produced by hot-pressing powder supplied by the London and Scandinavian Metallurgical Co. Ltd. Metallographic examination of the hot-pressed carbides showed them to be fine grained, with grain diameters of less than 100 µm. The arc cast uranium carbide was considerably coarser with a grain diameter of about 500 µm. All the carbides were apparently single phase, albeit some samples contained up to 1 or 2 at. % of "free" carbon as shown in Table I. The samples had densities of at least 98 % of the theoretical values and only small amounts of isolated porosity were observed during the metallographic studies. Before being used in the wetting experiments the carbide surfaces were ground parallel and polished on laps impregnated with 1 µm diamond paste.

All the metals employed were of Johnson Matthey spectroscopically pure quality. The alloys were prepared *in situ* by machining a cylinder of copper 3 mm in diameter and about 6 mm high, with a hole in the top face into which the required amount of alloying element was placed, the total weight of a cylinder plus alloying addition being 0.300 g. The samples were ultrasonically cleaned in methylated spirits before introduction into a vacuum furnace.

The furnace was evacuated to 1×10^{-5} torr and the samples outgassed by heating at 850 to 1050°C for 30 min, the particular temperature employed depending on the alloy melting point. The temperature was then raised rapidly to 1150°C and the sessile drop outline photographed at regular intervals for up to 7 h using a 35 mm Nikon camera. The wetting behaviour was defined by contact angle measurements from projected images of the film negatives.

When experiments were duplicated or stable drop configurations measured that had been photographed at different times, the contact angle values did not differ by more than ± 2°, which was also the estimated accuracy for individual measurements.

The final stage of the experimental procedure was to section and polish the samples to a 1 μm finish, using diamond-impregnated pads, for subsequent metallographic and electron probe microanalyser examination.

3. Experimental results

3.1. The effect of alloy concentration on the wetting of carbon

During the first few minutes of the experiments the contact angles between carbon and the alloy sessile drops changed rapidly with time as the active carbide forming additions dissolved. After about 15 to 20 min at temperatures, the drops assumed steady or very slowly changing contact angle values as illustrated by Fig. 2. The concentration of the alloying element affected the wetting behaviour of each of the three systems as shown by Fig. 3 which presents contact angle values measured after 2 h at temperature. A change from non-wetting to wetting behaviour occurred at concentrations of approximately 0.1 at. % for copper-chromium and copper-vanadium alloys on vitreous carbon substrates and 10 at. % for copper-titanium alloys on both vitreous carbon and HX30 graphite substrates.

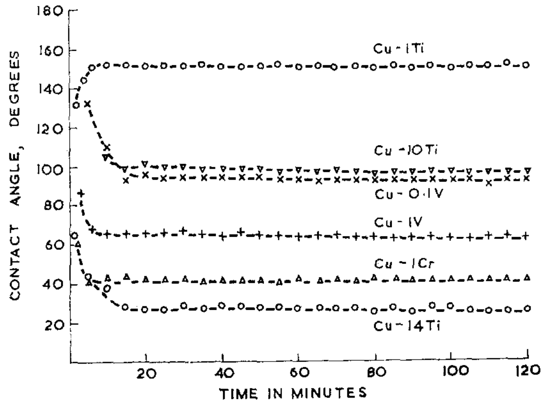

Figure 2 The variation with time at 1150°C of the contact angle between several copper alloy sessile drops and vitreous carbon.

The changes in wetting behaviour suggested that the carbide forming element had segregated to a liquid-solid interface and metallographic examination revealed that carbide layers were formed there. Alloys containing sufficient chromium or vanadium to noticeably affect wetting behaviour, i.e. more than 0.1 and 0.01 at. % respectively, had continuous adherent carbide layers present at the carbon-metal interfaces similar to those shown in Fig. 4. The copper-titanium alloys initially formed continuous carbide layers at the interfaces, Fig. 4, but after a time the morphology of the reaction product formed by the richer alloys changed and particulate zones were produced, Fig. 5. The interfacial morphology data summarized in Fig. 6 show that this change occurred in less than 2 h when alloys containing at least 3 or 10 at. % of titanium were contacted with HX30 graphite or vitreous carbon respectively. The thickness of both continuous layers and particulate zones increased with alloying concentration as shown in Figs. 7 and 8. These figures also show that the con-

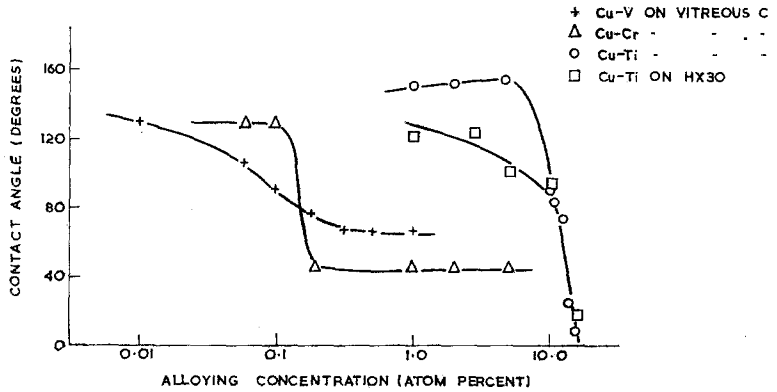

Figure 3 The effect of alloying concentration on the wetting of carbon by copper alloys.

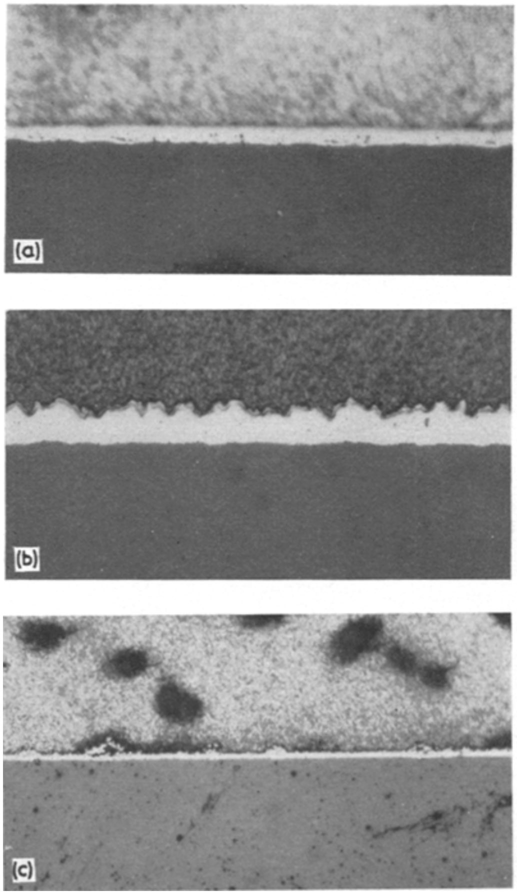

Figure 4 The appearance of interfaces between vitreous carbon and copper alloyed with 1 at. % of (a) chromium, (b) vanadium and (c) titanium. All the samples were held at 1150°C for 2 h and after metallographic preparation were etched in acidic $FeCl_3$ solution. × 360.

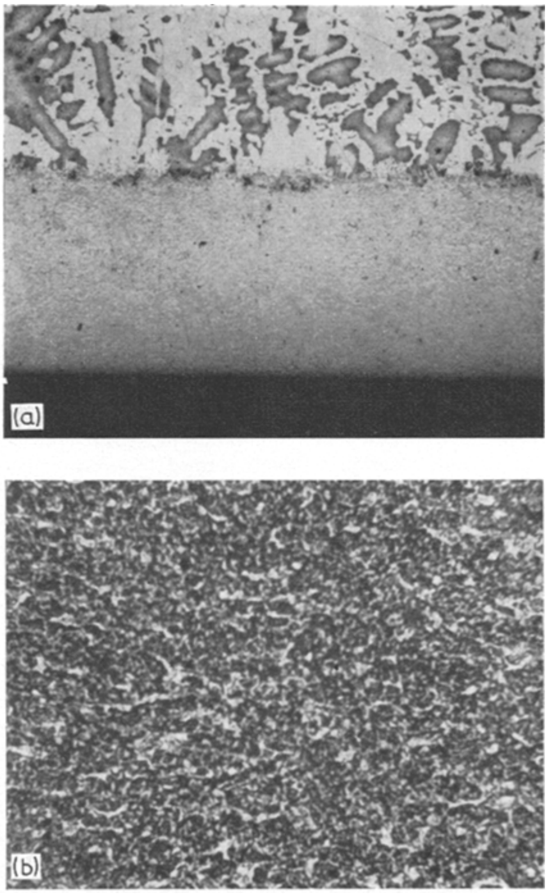

Figure 5 The appearance of interfaces formed between vitreous carbon and sessile drops of copper-15 at. % titanium held for 2 h at1 150°C, (a) general view at × 144, (b) particulate zone at × 1080.

tinuous layers thickened parabolically with time while the particulate zones thickened linearly.

3.2. Carbide substrates

Series of carbide wetting experiments were conducted using sessile drops of pure copper and copper alloyed with one or more carbide formers. As in the case of the carbon substrate experiments, the contact angle values stabilized after 15 to 20 min at temperature and Table II summarizes the stable values measured for the various systems after 1 h at temperature. The table shows that alloying with the carbide parent metal had only a slight effect on the wetting of most carbides but larger changes occurred with the copper-titanium and the ternary alloys.

Changes in wetting behaviour may be due to chemical interactions at the liquid/solid interfaces and evidence of this was sought from metallographic examination and electron probe microanalyser surveys of the solidified sessile drop samples. Optical microscope studies proved to be inconclusive, no interfacial zones of reaction product being revealed, possibly due to the thickness of any such zones being below the resolving power of the microscope or to their being very similar in colour and polishing behaviour to the parent carbide. The electron probe microanalyser surveys of many samples showed evidence of interfacial segregation of foreign carbide forming elements but no conclusive evidence of parent carbide forming element segregation. Even the observation of foreign element segregation was merely qualitative, the segregation zone widths being less

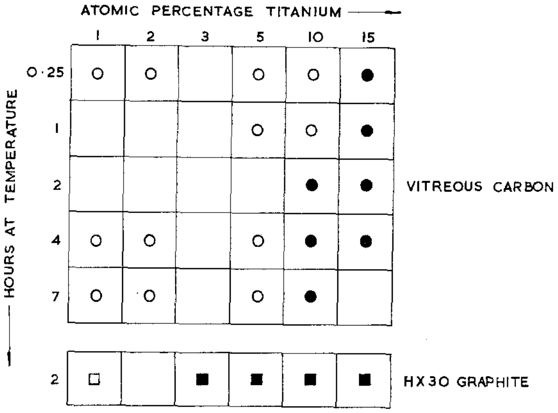

Figure 6 Schematic representation of the morphologies of the carbide reaction products formed between copper-titanium alloys and carbon substrates. Open symbols indicate continuous lays and full symbols indicate particulate zones.

than the 2 to 3 μm needed for their compositions to be analysed quantitatively. The segregation zone of this type with the greatest width, about 2 μm, was that formed by the copper-titanium/WC sample, and is shown in Fig. 9.

Equation 3 was used to obtain relative surface-energy values by substitution of the contact angle data presented in Tables II and III for binary alloy sessile drops resting on alloy carbide or carbon substrates. In calculating these values, the surface energies of the dilute alloys were assumed to equal that of copper in low oxygen environments [7], about 1.25 Jm^{-2} [8-10]. Absolute carbide surface energy values were derived by assigning a value of 0.72 Jm^{-2} for γ'_{UC} [11], although in fact this value is for the carbide in a contaminant free environment.

TABLE II Summary of contact angle measurements for carbide substrates

Pure copper

Substrate	Contact angle in degrees
Cr_3C_2	50
HfC	134
NbC	58
TiC	113
UC	122
VC	45
WC	17
ZrC	128

Binary alloys

Substrate	Alloy additions	Contact angle in degrees
Cr_3C_2	Cr	26
HfC	Hf	146
NbC	Nb	65
TiC	Ti	118
UC	U	124
VC	V	62
WC	W	10
ZrC	Zr	138
Cr_3C_2	Ti	120
NbC	Ti	0
WC	Ti	20

Ternary alloys

Substrate	Alloy additions	Contact angle in degrees
HfC	Hf + V	105
VC	Hf + V	58.5
NbC	Nb + W	56
WC	Nb + W	28
TiC	Ti + V	72
VC	Ti + V	46
VC	V + Zr	49.5
ZrC	V + Zr	112.5

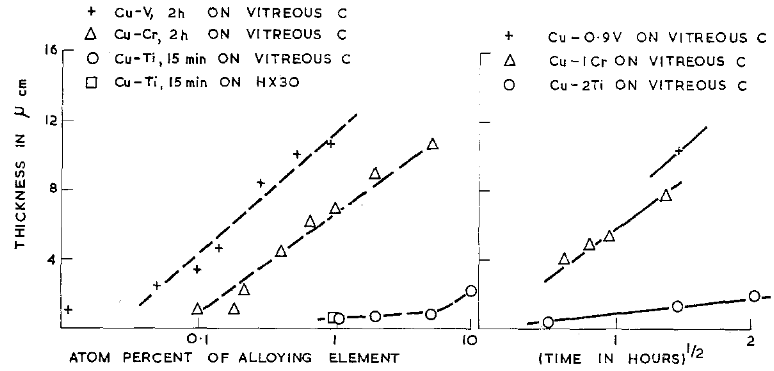

Figure 7 The effect of alloy concentration and time at 1150°C on the thicknesses of continuous interfacial carbide layers.

TABLE III Contact angle measurements for copper alloys on carbon quoted in [1]

Alloying addition	Contact angle in degrees
Cr	50
Hf	130
Nb	152
Ti	135
U	118
V	90
W	134
Zr	152

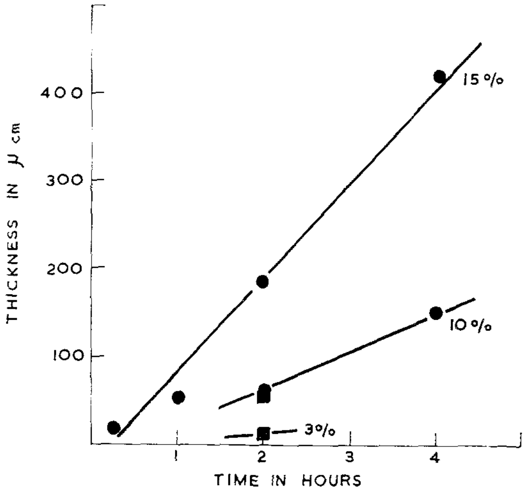

Figure 8 The effect of alloy concentration and time at 1150°C on the thicknesses of the particulate zones formed between carbon and copper-titanium alloys; ●vitreous carbon substrates, ■HX30 graphite substrates.

The results of these calculations are presented in Table IV.

4. Discussion

The data presented in the previous section are numerous and relate to many substrates. For the sake of clarity, the significance of the experimental results will be discussed in the sections below.

4.1. The effect of alloying concentration

The experimental results demonstrate that variations in the concentration of carbide forming alloying elements can have profound effects on the wetting behaviour and the morphology of interfacial reaction products formed between copper alloys and carbon. However, these changes do not occur at concentrations close to the 1 at.% level used in the study described in [1]. The nominal concentrations of chromium and vanadium can be changed from 0.15 at.% to 6 and 1 at.% respectively and that of titanium from 1 to 5 at.% without much

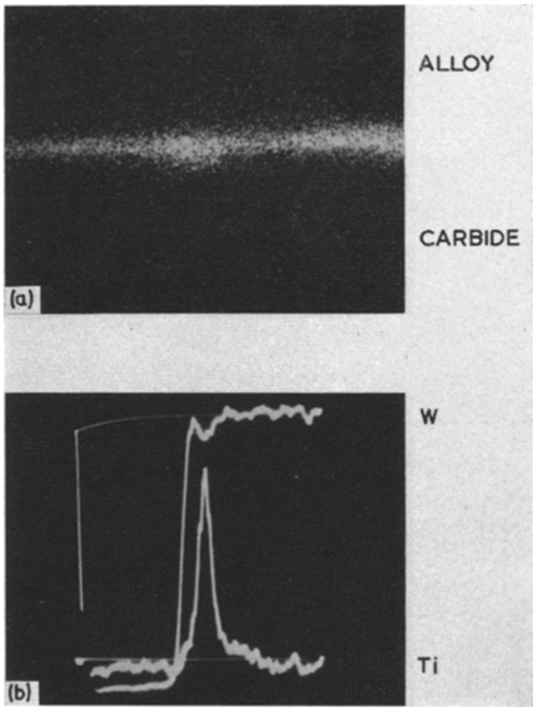

Figure 9 Electron probe microanalyser survey of the interface between a copper-titanium sessile drop and a WC substrate; (a) titanium X-ray image, (b) X-ray intensity trace, × 1500.

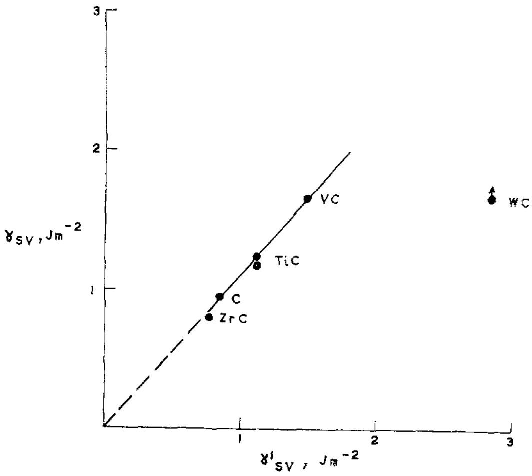

Figure 10 A comparison of γ'_{SV} values derived during this study with γ_{SV} values published in the literature.

TABLE IV Comparison of carbide surface energies derived from wetting data with literature values

	γ'_{XC} (Jm^{-2})		Literature values	
	As calculated	Adjusted	γ_{XC} (Jm^{-2})	γ_{XCcrit} (Jm^{-2})
	Calculated from (Cu + X)/XC data			
Cr_3C_2	1.14	1.07		
HfC	0.61	0.54		
NbC	2.40	2.33		
TiC	1.12	1.05	1.19 [12], 1.24 [13]	1.08 [13]
VC	1.40	1.33	1.67 [12]	
WC	2.85	2.78	1.67 [12]	
ZrC	1.00	0.93	0.80 [12]	
C	0.83	0.76	0.99 [14]	
	Calculated from (Cu + Ti)/XC data			
Cr_3C_2	1.08	1.01		
NbC	2.88	2.81		
WC	2.81	2.74		
	Calculated from (Cu + X + Z)/XC data			
HfC(VC)	0.64	0.57		
VC(TiC)	1.58	1.51		
ZrC(VC)	0.55	0.48		

affecting the contact angle values or, by implication, the interfacial energies.

There was no systematic study of the effect of alloying concentration on the wetting behaviour of carbides, but it is interesting to note that the contact angle values for pure copper and copper alloyed with 1 at.% of the carbide parent metal were usually very similar. This also indicates that small changes in interfacial chemistry have only minor effects on energy values and validates the use of pure copper wetting data in [1] to analyse the behaviour of alloy/carbon systems.

The effect of titanium concentration on wetting behaviour at first sight does not seem to be explicable in terms of the model described in the introduction. However, in order to test fully the validity of the model, values for the contact angles between TiC and a range of copper-titanium alloys were measured. Increasing the titanium concentration of copper alloys from 1 to 13 at.% decreased their contact angles with TiC at 1150°C from 118° to less than 10°. Substitution of these angles and literature values for the surface energy of TiC [12] and molten copper-titanium alloys [7] into Equation 1 showed that the change was due to a decrease in the interfacial energy from 1.78 to 0 Jm^{-2}. An equal decrease in the energy of the alloy/carbon interfaces, as predicted by the model, would reduce the contact angle from 152° to 58°. The similarity of this reduction to that observed in practice, 152° to 72°, demonstrates that the model is in fact applicable to copper alloys containing both low and high concentrations of titanium provided relevant contact angle data are used.

Titanium concentration also has an effect on the morphology of the reaction products formed with carbon substrates. However, the effects on wetting and carbide morphology are independent phenomena. Thus Fig. 3 shows that an alloying concentration of 10% is needed to induce copper to wet graphite whereas Fig. 6 shows that 3% is sufficient to change the morphology of the reaction product. The change in the morphology of the titanium carbide reaction product shown in Figs. 4 and 5 is similar to that observed when an oxide film undergoes "breakaway" due to interfacial decohesion. The conditions under which this change occurs are different for vitreous carbon and graphite substrates, perhaps reflecting the greater strength and lower porosity of vitreous carbon. Once the change in interfacial morphology occurs, the thickness of the zone of titanium carbide particles is proportional to the contact time and such "linear" growth is characteristic of oxide films that have undergone breakaway.

4.2. The use of wetting data to derive carbide surface energies

Table IV compares the γ'_{XC} values calculated from contact angle data for alloy/carbide systems with surface energies previously published by Livey and Murray [12] and Rhee [13, 14]. Livey and Murray's values are for γ_{XC} while Rhee quotes values for both γ_{XC} and the critical surface energy, γ_{XCcrit}, which is equal to $\gamma'_{XC} - \gamma_{sl}$ when the contact angle is zero, where γ_{sl} is the solid/liquid interfacial energy. In practice it has been found that γ_{XCcrit} is similar to but slightly smaller than γ_{XC}. The new data presented in Table IV and in Fig. 10 are in good agreement with published figures for carbon and the carbides, TiC, VC and ZrC, for which a comparison can be made, the γ'_{XC} values being about 10% smaller than the γ_{XC} values. Adjusting the γ_{UC} substandard value by this amount yields a γ'_{UC} of 0.65 Jm^{-2} and reduces the other calculated γ'_{XC} values by about 0.07 Jm^{-2}.

Having achieved some success in analysing the (Cu + X)/XC wetting data an attempt was made to treat the copper-titanium alloy and the ternary alloy data. There is evidence of titanium segregation to alloy/carbide interfaces and hence the possible formation of titanium carbide. Table IV presents surface energy values derived from copper-titanium alloy wetting data using the previously calculated value of 1.05 Jm^{-2} for γ'_{TiC} as a substandard. Analysis of the ternary alloy wetting data presented in Table II is more difficult since the compositions of the carbide/alloy interfaces cannot be identified. However, if it is arbitrarily assumed that a pair of carbides, XC and ZC, form energetically similar interfaces with the ternary alloy (Cu + X + Z), the same type of analysis can be attempted. Several different substandards have to be used to calculate apparent surface energies in this attempt. The results of these calculations, and the identity of the substandard, are presented in Table IV.

These new surface energy values are reasonably self consistent and in good agreement with data calculated from the wetting behaviour of (Cu + X)XC systems. This comparison of values suggests that the model can be applied to a wide range of carbide substrate systems and that contact angle measurements which are simple to obtain experimentally can be used as a guide to solid surface energy values.

5. Concluding remarks

Analysis of both the carbon and the carbide wetting data presented in this paper indicate that the very simple model developed initially to describe the wetting behaviour between carbon and copper alloyed with 1 at.% of various carbide formers can be applied even when different alloying concentrations and carbon containing substrates are used. The reason for this wider applicability is probably the insensitivity of interfacial energy values to minor changes in the chemistry of reaction product carbide layers. This enables the energy values to be predicted with reasonable accuracy even though the detailed interfacial chemistry is not known. Even when concentration variations are such that changes in wetting behaviour and presumably interfacial chemistry do occur, as with the 13 at.% titanium alloy, the model can still be used as a guide to surface energy values providing relevant wetting data are used. Whether the model can be applied to other ceramics such as oxides has yet to be shown.

Acknowledgements

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