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The wetting and bonding of diamonds by copper-base binary alloys

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The wetting and bonding behaviour between diamond plaques and copper alloyed with chromium, titanium or vanadium has been studied using the sessile drop technique. Wetting was induced at 1150° C by additions of more than 0.1 at.% of titanium, but additions of vanadium up to and beyond the solubility limit did not cause wetting to occur. The room temperature strengths of the interfaces between the diamond plaques and the solidified sessile drops increased with increasing alloying element concentration, reached a maximum value at a concentration less than that needed to induce wetting, and thereafter decreased. The maximum strengths achieved by alloying with chromium, titanium or vanadium were 35.5, 42.0 and 69.8 kg mm^{-2} respectively. The reactivity of the alloyed sessile drops was assessed using metallography, EPMA and a surface contour device. A tentative picture of the effects of diamond–metal interactions on wetting and bonding behaviour was developed.

1. Introduction

The development of brazes for single point diamond tools or liquid infiltrants for the production of metal bonded diamond grit compacts is difficult because not only must wetting and bonding criteria be satisfied but also the fabrication process must not result in excessive loss of diamond due to chemical interaction with the metal or reversion to the more stable graphite. Many commercial brazes are based on copper alloys but copper itself does not wet or bond well to diamonds or to other forms of carbon since only weak van der Waal's forces operate across the interfaces. Alloying the copper with carbide forming elements sometimes can promote its wetting of carbon, including diamonds [1–5], but there is little equivalent information describing the effects of such alloying behaviour on diamond–metal bonding. The specific objectives of the programme were to relate the effects of alloying concentration on wetting behaviour, diamond–metal chemical interactions and bonding and hence to formulate a more general understanding of factors of importance in the selection of brazes and infiltrants.

The programme employed copper alloyed with chromium, titanium or vanadium, the additions being chosen because they are known to promote the wetting of some forms of carbon. The sessile drop technique, in which the contact angle between a liquid drop and the horizontal solid substrate on which it rests is measured, was used to study wetting behaviour. The contact angle, θ, subtended at the periphery by the liquid surface and the solid–liquid interface is determined by the interplay of the various surface energies which are related by the Young–Dupré equation

$$\gamma_{SV} = \gamma_{LV} \cos\theta + \gamma_I$$

where γ_{SV} is the solid substrate–vapour surface energy, γ_{LV} is the liquid–vapour surface energy and γ_I is the interfacial energy between the liquid metal and solid substrate. The practical significance of the angle is that it must be less than 90°

if a liquid is to freely spread over a solid surface or penetrate capillaries in, say, a powder compact. The bonding characteristics of the various alloy–diamond systems were assessed at room temperature using the Sutton "push-off" test. Previous work [6] has shown that solidified specimens with "contact angles" greater than 107° failed in tension and that the interfacial tensile strength U was given by

$$U = 4\frac{L}{A}\tan(\alpha - 90^\circ)$$

where L was the applied load at which separation occurred, A was the interface area, and α was the "contact angle" of the solid drop at room temperature. Specimens with "contact angles" of less than 107° failed in shear and the shear strength S was calculated simply from the failure load and contact area, and converted to a tensile strength by arbitrarily multiplying by 1.25.

2. Experimental materials and techniques

Diamond plaques with polished surfaces oriented to within ± 2° of the (1 1 1) plane were supplied by the De Beers Industrial Diamond Division. Copper alloys containing chromium, titanium or vanadium were prepared either by argon arc melting of spectroscopically pure metals or *in situ* during the sessile drop experiments [4]. The sessile drop samples were prepared as 1 mm diameter cylinders weighing 0.0375 g.

The wetting experiments were carried out in a vacuum furnace at a temperature of 1150 ± 10° C and a pressure of about 6×10^{-3} N m^{-2} after first degassing the samples for 1 h at 900° C (or 600° C in the case of the copper–titanium alloys). The sessile drop outline was photographed at regular intervals with a 35 mm camera for 20 min from the moment the drop was completely molten, after which it was cooled to room temperature. Equilibrium as defined by a constant contact angle was generally attained in under 10 min. Contact angles were measured from the film negatives projected onto the screen of a Nikon Profile Projector.

The interfacial bond strengths between the solidified sessile drops and the diamond plaques were determined using a Hounsfield Tensometer, the samples being held in a shearing jig. The dimensions of the detached drops were measured with a travelling microscope to determine the interface areas and the "contact angles" of the solid drops.

The separated diamond plaques were examined with a modified Talystep I direct contact stylus instrument to determine the contour of the fracture surfaces both before and after chemical removal of any adherent product carbide layers. Electron probe microanalysis techniques were used to determine the composition of any materials adhering to the fracture surfaces of diamonds or solidified drops. A small number of detached sessile drops were sectioned and polished for metallographic examination.

3. Results

Several series of experiments were conducted and the results of each main series of experiments are presented separately.

3.1. Copper–chromium alloys

The wetting behaviour of copper–chromium alloys contacted with diamonds for 20 min at 1150° C is summarized in Fig. 1. Wetting occurred at chromium concentrations in excess of 0.1 at. %.

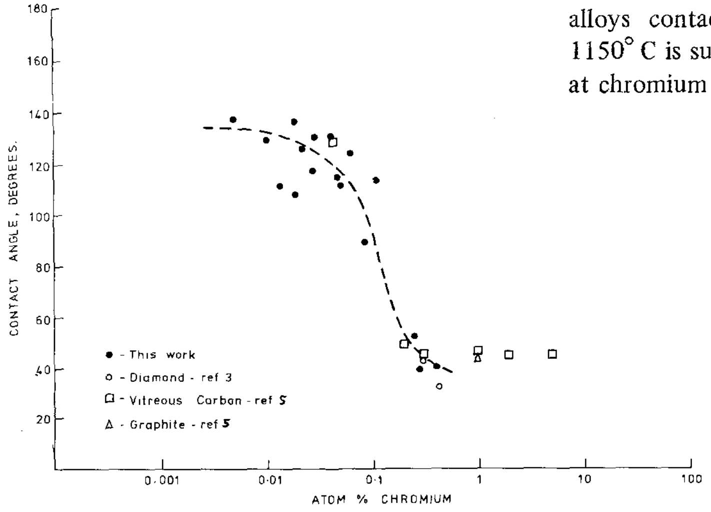

Figure 1 Wetting behaviour between copper–chromium alloys and diamond plaques.

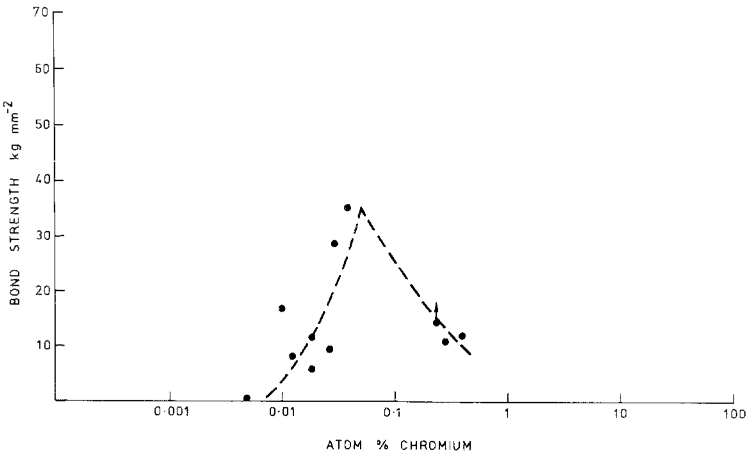

Figure 2 Bonding behaviour between solidified copper–chromium sessile drops and diamond plaques.

The experimental results are reasonably self-consistent and in fair agreement with literature data for copper–chromium alloys in contact with diamonds, vitreous carbon and graphite [1–5]. The interfaces between the solidified sessile drop and the diamond could be viewed through the back of the diamond plaques and whereas pure copper had formed a bright shiny interface, the copper–0.005 at.% chromium alloy formed a patchy dark coloured interface. Alloys appreciably richer in chromium formed uniform dark coloured interfaces.

The 0.005 at.% chromium alloy sample did not adhere to the diamond on solidification. The effect of increasing the chromium concentration above this level was to increase the bond strength up to a maximum value of 35.5 kg mm^{-2} for a 0.037 at.% alloy but further additions of chromium caused the bond strengths to decrease as shown in Fig. 2.

Electron probe microanalysis using low electron beam energies of some of the diamond fracture surfaces showed them to be enriched in chromium by a factor of four or five hundred times the bulk metal chromium concentration and it was inferred that carbide had been formed at the interfaces. Metallographic examination of the detached drop containing 0.40 at.% chromium showed a continuous adherent layer 1.75 μm thick (Fig. 3). Talystep contour surveys of the diamond fracture surfaces showed that solidified drops containing 0.1 at.% chromium or less had failed above the surrounding unreacted diamond surface presumably at or near the metal–carbide interface. Drops with more than 0.1 at.% chromium failed below the surrounding diamond surface within the carbide layer. After the adherent carbides had been cleaned off the diamonds further Talystep surveys revealed erosion pits whose average depths varied from 0.01 to 0.25 μm, increasing with increasing chromium concentration, although it was difficult to estimate average erosion depths produced by the leaner alloys. Fig. 4 presents some of the traces obtained for this series of samples. Reaction product thicknesses calculated from the erosion depths by assuming an interface composition of Cr_3C_2 were in reasonable agreement with the result of a metallographic examination of one of the richer alloys, and the thicknesses inferred for the leaner alloy samples from the changes in Talystep contours produced by cleaning the diamond surfaces (Table I).

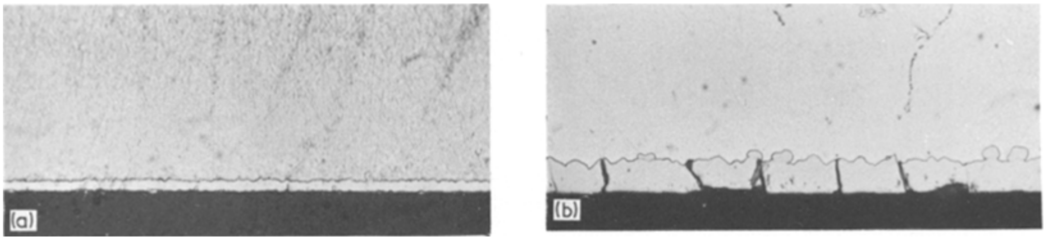

Figure 3 Metallographic appearance of cross-sectioned fracture surfaces of solidified sessile drops of (a) a copper–0.40 at.% chromium alloy and (b) a copper–1.03 at.% vanadium alloy, × 800.

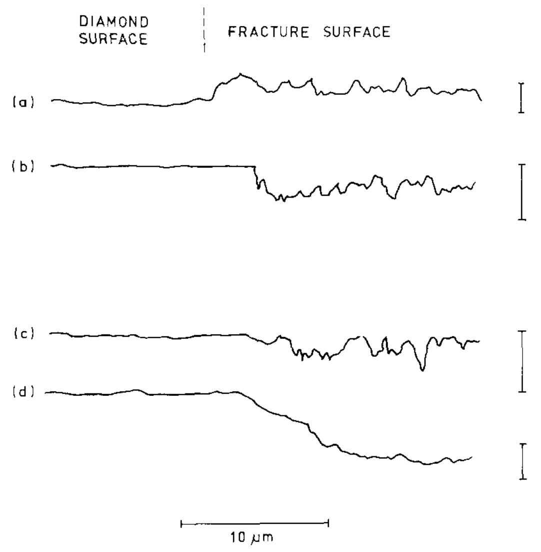

Figure 4 Talystep traces showing diamond fracture surface contours before and after cleaning for plaques contacted with a copper–0.015 at.% chromium alloy, (a) and (b), and a copper–0.27 at.% chromium alloy, (c) and (d). Vertical bars corresponding to heights of 0.10 µm.

TABLE I Interfacial carbide layer thicknesses

	Alloy concentration (at. %)	Etch depth (µm)	Calculated thickness (µm)	Measured thickness (µm)
Cu/Cr	0.01	0.01	0.08	0.09(T)
	0.105	0.02	0.16	0.12(T)
	0.40	0.25	1.98	1.75(M)
Cu/Ti	0.032	0.05	0.20	0.10(T)
	0.054	0.02	0.08	0.17(T)
	0.088	0.03	0.12	0.18(T)
Cu/V	0.0013	0.05	0.17	0.10(T)
	0.008	0.10	0.34	0.15(T)
	10.2	1.1	3.8	6.0(M)

(T) Measured interfacial layer thicknesses inferred from Talystep contour surveys of the diamond fracture surfaces before and after chemical removal of adherent carbides.

(M) Measured interfacial layer thicknesses from metallographic sections of detached solidified sessile drops.

3.2. Copper–titanium alloys

The contact angle and bond strength values obtained using copper–titanium alloys are shown in Figs. 5 and 6. Wetting occurred only at the highest titanium concentration, 15 at.%, in general agreement with other workers' observations [1–5]. This wetting sessile drop fell off the diamond plaque as it was removed from the furnace. The strongest bonding, 42 kg mm^{-2}, was produced by an alloy containing 0.040 at.% titanium and frequent small scale damage of the diamond plaques occurred as a result of the strength tests on the non-wetting sessile drops.

The optical appearance of the fracture surfaces on the diamond produced by the titanium rich alloys was uniformly rough while rather patchy interfaces were visible with the leaner alloys (Fig. 7). Electron probe microanalysis of the fracture surfaces of diamonds which had been in contact with the alloys containing 1.05 and 10.0 at.% titanium revealed small residual amounts of copper and titanium. A special electron probe technique employing various beam voltages was used on the detached 15.0 at.% titanium sessile drop. At the lowest electron energy of 8 kV, when the depth of penetration of the electrons was calculated to be

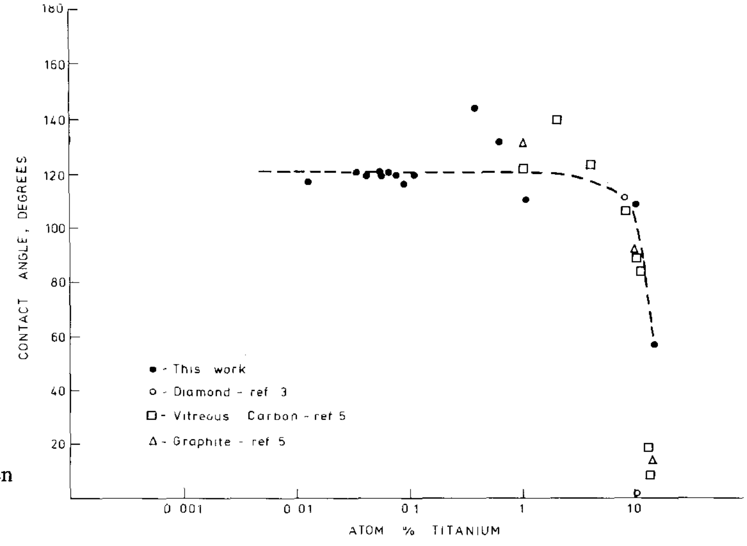

Figure 5 Wetting behaviour between copper–titanium alloys and diamond plaques.

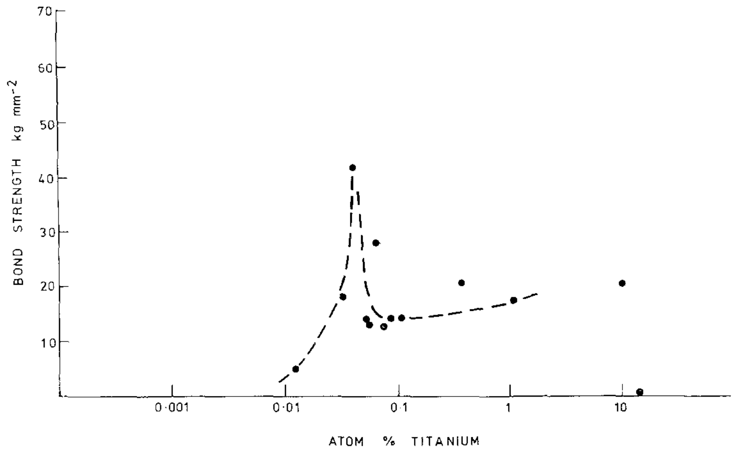

Figure 6 Bonding behaviour between solidified copper– titanium sessile drops and diamond plaques.

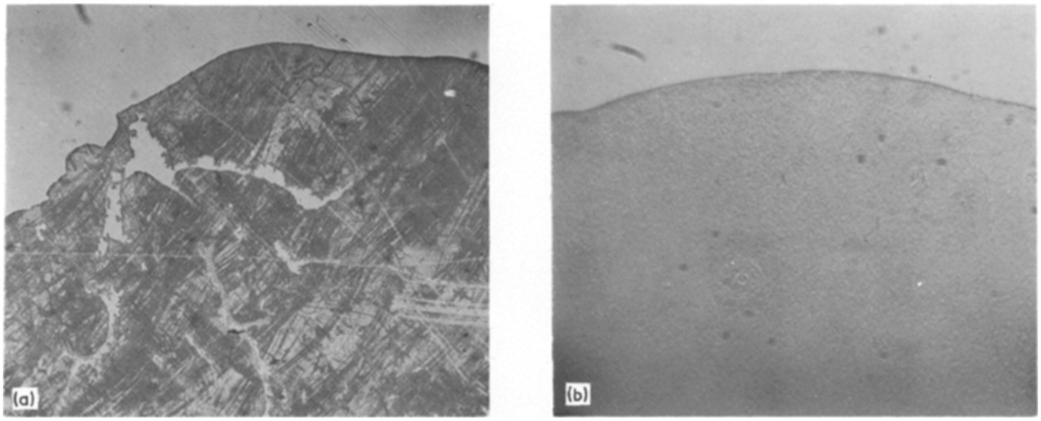

Figure 7 Optical appearance of interfaces formed between diamond plaques and (a) a copper–0.013 at. % titanium alloy and (b) a copper–15 at. % titanium alloy, X 64.

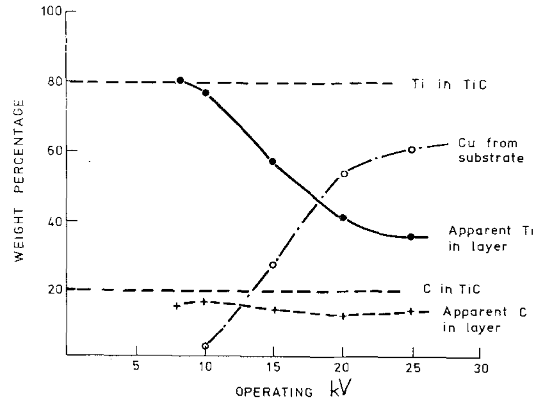

Figure 8 Titanium, carbon and copper concentrations at the fracture surface of a copper–15 at. % titanium sessile drop as a function of electron microprobe analyser beam energy.

approximately 0.37 μm, the X-ray intensities from titanium and carbon were amost the same as from a specimen of titanium carbide as shown in Fig. 8. Further evidence of the formation of carbide layers was obtained from metallographic examination of detached sessile drops containing 1.05 and 15.0 at. % of titanium, small fragments of a sub-micron layer being visible in the case of the 15.0 at. % alloy.

The fracture surfaces of many of the separated diamond plaques were surveyed by the Talystep I instrument both before and after being cleaned. While most of the fracture surfaces were higher than the surrounding diamond there was an indication that titanium rich samples (above about 0.06 at. %) fractured below the diamond surface. The depths or erosion determined on the cleaned diamonds were comparatively shallow. Again there was a reasonable correlation between interfacial layer thicknesses calculated from erosion depths and thicknesses inferred where possible from the Talystep surveys (Table I).

3.3. Copper–vanadium alloys

Figs. 9 and 10 summarize the wetting and bonding results obtained for copper–vanadium alloys, none of which wetted diamond. All the solidified sessile drops adhered to the diamond plaques, the best result being an interfacial tensile strength of 69.8 kg mm^{-2} obtained when an alloy containing 0.0061 at.% vanadium was used. It was apparent from the sessile drops containing 1.03, 5.13 and 10.2 at.% that all the vanadium had not dissolved and that these were, therefore, two phase alloys under our experimental conditions.

Observation of the interfaces showed that as in the other alloy systems, lean alloys formed patchy interfaces and rich alloys formed uniformly discoloured interfaces. Metallography on the detached sessile drop containing 10.2 at.% vanadium showed an interfacial layer 7 μm thick (Fig. 3). Electron probe microanalysis of the interfacial layer attached to the sample containing 1.03 at.% vanadium revealed near stoichiometric vanadium carbide. Talystep surveys of the diamond fracture surfaces showed that samples containing not more than 0.008 at.% vanadium fractured above the diamond surface while samples containing more than 1.03 at.% vanadium fractured below the surrounding unreacted diamond surface. The erosion depths varied from 0.03 to 1.1 μm for the lowest to highest vanadium concentration and again quite good agreement was obtained between measured interface thicknesses and those calculated from the amount of diamond eroded assuming complete conversion to stoichiometric vanadium carbide (Table I).

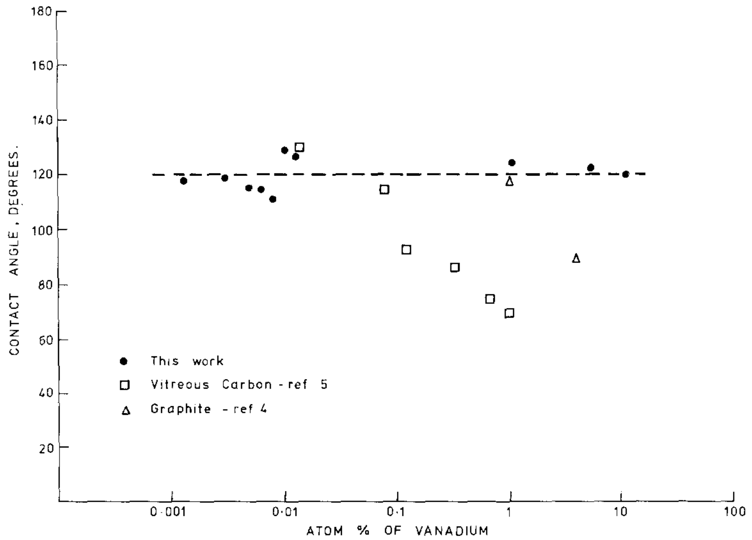

Figure 9 Wetting behaviour between copper–vanadium alloys and diamond plaques.

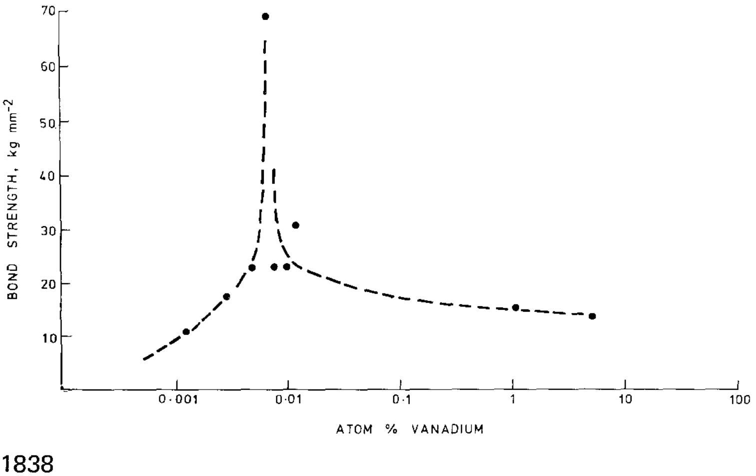

Figure 10 Bonding behaviour between solidified copper–vanadium sessile drops and diamond plaques.

4. Discussion

The objective of this work was to define the wetting and bonding behaviour between diamond and copper based alloys containing chromium, titanium or vanadium. All three binary alloy systems are known to wet graphite and vitreous carbon at certain concentration levels [1–5]. A comparison of the results of the present work with published wetting data of the three binary alloys on diamond vitreous carbon and graphite at 1150° C is given in Figs. 1, 5 and 9. Most published data on the wetting of diamond [1, 3] agree quite well with our results. This is also true for the copper–chromium and copper–titanium alloys in contact with graphite and vitreous carbon. The discrepancy in the wetting behaviour of copper–vanadium alloys on diamond and vitreous carbon is marked and inexplicable at present.

The electron probe measurements on some of the broken metal–diamond interfaces showed migration of the added transition element to the interface and the presence of near stoichiometric carbides in the case of titanium and vanadium containing alloys. The wetting of vitreous carbon graphite by copper based alloys containing carbide forming additions has been interpreted in terms of the surface energies of the substrate and the stable stoichiometric reaction product carbides at the metal–carbon interface [4]. The similarity between diamond and graphite wetting behaviour suggests that the diamond surface energies are also about 1 $\mathrm{J\,m^{-2}}$

The most notable feature of the interfacial strength measurements made during this work is the high strengths produced by alloys with compositions falling within certain very narrow concentration ranges. These optimum concentrations are considerably less than those needed to induce changes in wetting behaviour, and the maximum interfacial strength values achieved do not correlate with the reactivity of the alloying elements, in contrast to the observations made previously with metal–alumina systems [7]. Neither do the room temperature interfacial strength measurements correlate with the thermodynamic work of adhesion values (equal to γ_{LV} $[1 + \cos\theta]$).

The Talystep measurements, metallographic examination of some of the detached sessile drops and electron probe microanalysis indicated that fracture within the carbide close to the diamond surface occurred with the higher concentration sessile drops. Lower concentration drops fractured above the diamond surface suggesting that separation had occurred at or near the metal–carbide interfaces. The delineation of these fracture modes appears to be at the concentrations of alloying addition similar to those producing the peak strengths. Estimates of 0.16, 0.08 and 0.10 μm were made for the thicknesses of the reaction product layers at the strongest interfaces formed by copper alloyed with chromium, titanium or vanadium respectively. The similarity of these values suggest that some physical change occurs when carbide layers are about 0.1 μm thick.

These observations suggest a tentative picture of the diamond–metal bonding process. Diamond–copper interfaces are weak because no chemical interactions occur and bonding is due to van der Waal's forces only. However, when a diamond is contacted with an alloy, islands of carbide nucleate at favoured sites on the diamond surface. These islands, which may be epitaxial, strengthen the sample interfaces because carbides form a chemical bridge between the diamond and the metal. Increasing the concentration of the reactive element in the alloys causes more and/or larger carbide islands to form and hence the sample interface to become stronger. As the concentration of the carbide former is increased the islands of carbide grow, contact each other and form a continuous interfacial layer. After this point is reached, the interfaces cease to strengthen and may weaken as the carbide thickens due to the development of flaws or even porosity.

In practical terms, the work has shown that the addition of chromium, titanium or vanadium can improve both the wetting and bonding behaviour between diamonds and copper. These additions also produce erosion due to the formation of carbide layers. However this is quite slight, only 0.01 to 0.03 μm for the alloys forming the strongest bonds which contained 0.037 at.% of chromium, 0.040 at.% of titanium or 0.0062 at.% of vanadium. These optimum concentrations are far less than those needed to induce wetting and thus there are technical problems in utilizing the most strongly bonding alloys as a diamond compact matrix. The best compromise between wetting and bonding behaviour identified in this work seems to be the 0.24 at.% chromium alloy which had a contact angle of 53° and formed bonds with strengths of more than 14.8 $\mathrm{kg\,mm^{-2}}$.

Acknowledgements

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