The solid phase bonding of copper, nickel and some of their alloys to diamonds

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The bonding achieved by vacuum hot-pressing cylinders of copper, nickel and a few of their alloys against diamond plaques has been measured. Alloying with carbide-forming elements such as titanium can have a markedly beneficial effect on the bonding of copper and, to a lesser extent, of nickel. The strengths obtained also depended on the fabrication time and temperature, at first increasing and then decreasing with time. These phenomena are compared to those observed previously in a study of bonding between diamonds and molten copper alloys. Some evidence is presented that relates the phenomena to the abrasiveness of diamond grit compacts.

1. Introduction

A continuing programme has been undertaken to investigate some of the factors that control the strengths of bonds formed between diamonds and metals or alloys, the quality of which can play a significant role in determining the performance of both single point diamond tools and metal matrix diamond grit abrasive compacts. Such bonds can be formed by many techniques, but principally by using molten metals or alloys to wet and flow over diamond surfaces, by cold or hot-pressing mixtures of diamond grit and metal powders, or by electrolytic, chemical- or vapour-deposition processes. A recent article [1] described an evaluation of bonds formed by molten binary copper alloys and this paper describes an extension of that work to include interfaces formed with solid copper and copper alloys and also with nickel and nickel alloys.

The most notable feature of the liquid-phase bonding study was the effect of variations in the alloying concentrations of the carbide-forming elements, chromium, titanium and vanadium. The room temperature bond strengths increased with alloying element concentration, reached maximum values of 35.5, 42.0 and 69.8 kg mm^{-2} with additions of 0.037 at.% chromium, 0.040 at.% titanium, and 0.006 at.% vanadium, respectively, and thereafter decreased. The beneficial effects of these elements were related to the formation of thin continuous layers of carbide reaction products at the metal diamond interfaces and, therefore, should be achievable to some degree by solid as well as molten alloys. That this is so is implied by the many instances in the patent literature in which the use of mixtures of alloys containing carbide-forming elements is recommended as a means of producing abrasive compacts by hot or cold-pressing and then sintering mixtures of diamond grit and metal powder. There is, however, little scientific evidence that strong interfaces are indeed produced by cold- or hot-pressing alloys containing carbide-forming elements against diamonds, except for that cited in [2–4].

The general objective of the work described in this paper was to assess whether there was any similarity in the effects of small amounts of carbide-forming elements on the strengths of diamond–metal interfaces formed by liquid and solid-phase bonding processes. The specific objec-

tive was to determine the strengths of bonds formed with copper, nickel and copper or nickel alloys by hot-pressing as a function of fabrication time and temperature. Copper was chosen as a solvent metal because of its chemical inertness towards diamonds, and nickel because of its ability to interact through dissolution, as in diamond synthesis. Since the rate of formation of carbide reaction products at the diamond surfaces was thought to be critical, and the bonding temperatures employed were low relative to the melting points of the carbides, most of the alloys contained significant concentrations of the carbide-forming elements although the solid solubility limits were never knowingly exceeded.

2. Experimental materials and techniques

Various types of bonding experiments were performed using copper or nickel and alloys formed by them with chromium, titanium, vanadium or boron, by co-melting appropriate mixtures of spectroscopically pure metals either by resistance or arc heating in argon atmospheres. Ingots of the various alloys and spectroscopically pure copper and nickel were swaged to produce 1.5 or 3.0 mm diameter rods from which small cylinders 2.0 or 4.0 mm high were cut off using a watchmaker's lathe. The polished diamond plaques against which these cylinders were later pressed were supplied by the De Beers Industrial Diamond Division with surface orientations within $2°$ of the $(1\ 1\ 1)$ plane.

The diamond and metal samples were cleaned by ultrasonic agitation in methylated spirits and then hot-pressed together. After some initial trials, the standard bonding procedure adopted was to press at $800°C$ in a simple vacuum chamber using applied loads that exerted pressures of $3.6\ kg\,mm^{-2}$ on copper–, nickel– and copper alloy–diamond interfaces and $5.8\ kg\,mm^{-2}$ on nickel alloy–diamond interfaces. The vacuum chamber consisted of a 60 mm silica tube clamped top and bottom between neoprene inserts in water-cooled brass plates. The bottom plate had a passageway through which the chamber was evacuated and the top plate a Wilson seal through which passed a 25 mm diameter silica ram. The temperature of a metal cylinder-diamond plaque sample placed between the ram and a graphite anvil was raised to $800°C$ within 10 min by induction heating and a load was then applied to plastically deform the metal.

Interfacial bond strength tests were carried out on all specimens that adhered using a Hounsfield Tensometer attachment that has been described previously [5]. The bond strengths presented later were calculated directly from the fracture load and interfacial contact area.

In addition to this work with cylinders and plaques, a few samples were fabricated by hot-pressing diamond grit into the surfaces of metal alloy discs using a graphite die. These samples were later used to abrade sheets of EN2 steel lubricated with Super-edge No 7 water-based coolant. The abrasive performance of the samples was assessed in terms of their grinding ratios, the weight loss of the EN2 workpiece divided by the weight loss of the sample.

The diamond plaque–metal cylinder interfaces were examined prior to their fracture by viewing with an optical microscope through the backs of the plaques. After fracture, the diamond surfaces were re-examined using optical and scanning electron microscopy. In addition, a Talystep I direct contact stylus instrument was used to measure fracture surface profiles before and after the diamond plaques had been chemically cleaned to remove any attached metal or carbide reaction products. The diamond grit–metal disc samples were examined before and after their use in the abrasion tests by scanning electron microscopy.

3. Experimental results

Hot-pressing copper and copper alloys at $800°C$ with a force of $3.6\ kg\,mm^{-2}$ always produced complete metal–diamond contact in so far as viewing through the backs of the diamond plaques could indicate. Contact between the diamond plaques and nickel or nickel alloys, however, was often incomplete with, as will be mentioned in detail later, evidence that machining contours on the metal bond faces had not been completely removed.

Figs. 1 and 2 summarize the effect of variations in the diration of hot-pressing on the strengths of such interfaces formed by the pure metals and alloys. In the case of nickel and the various alloys, the strengths increased, reached a maximum value and then decreased with increasing duration of hot-pressing. This effect is similar to that observed previously with variations in the concentrations of carbide-forming elements present in molten copper alloys [1]. The maximum bond strengths achieved with copper alloys in the present work,
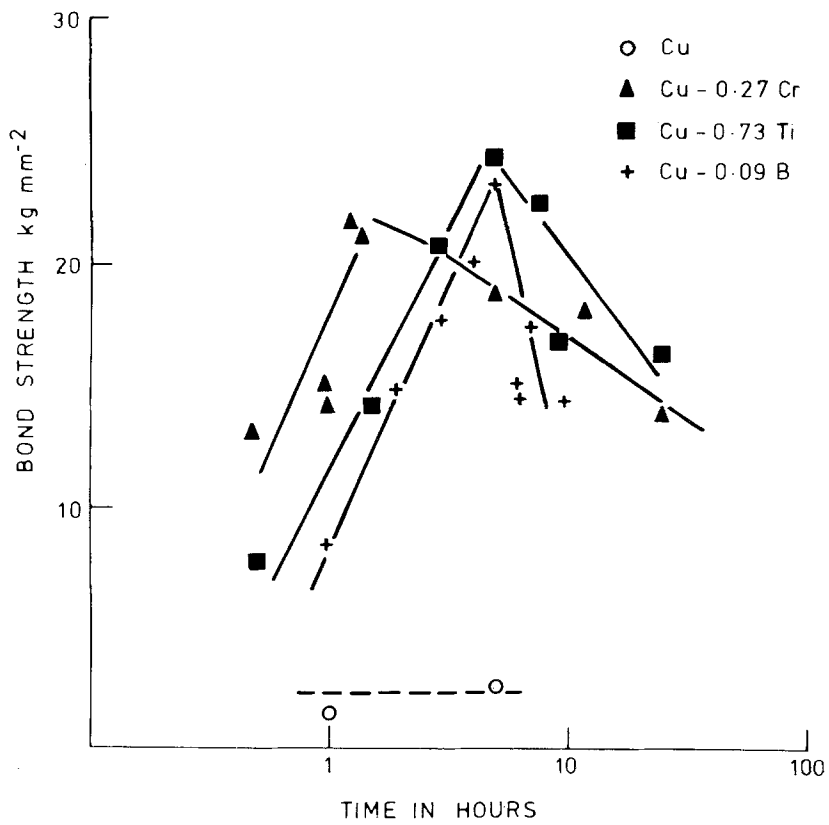
Figure 1 The effects of carbide alloying additions and fabrication time on the bonding of copper to diamonds.
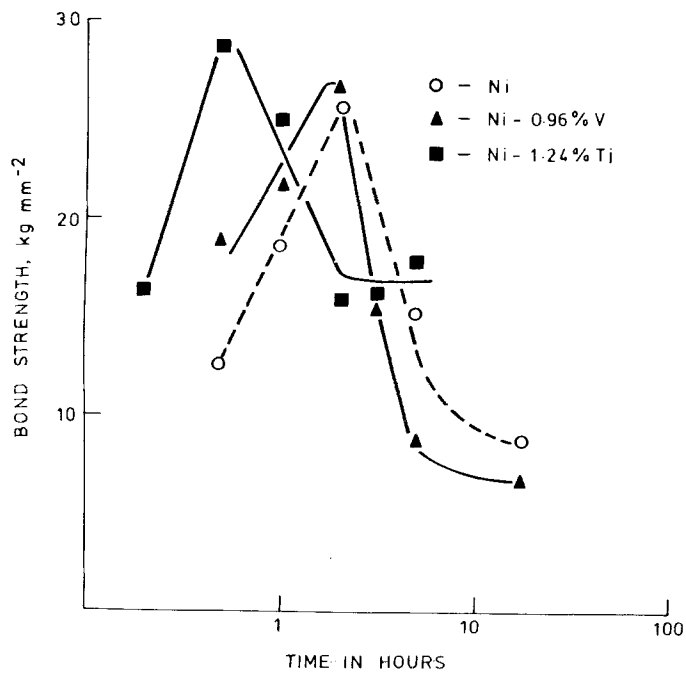

Figure 2 The effects of carbide alloying additions and fabrication time on the bonding of nickel to diamonds.
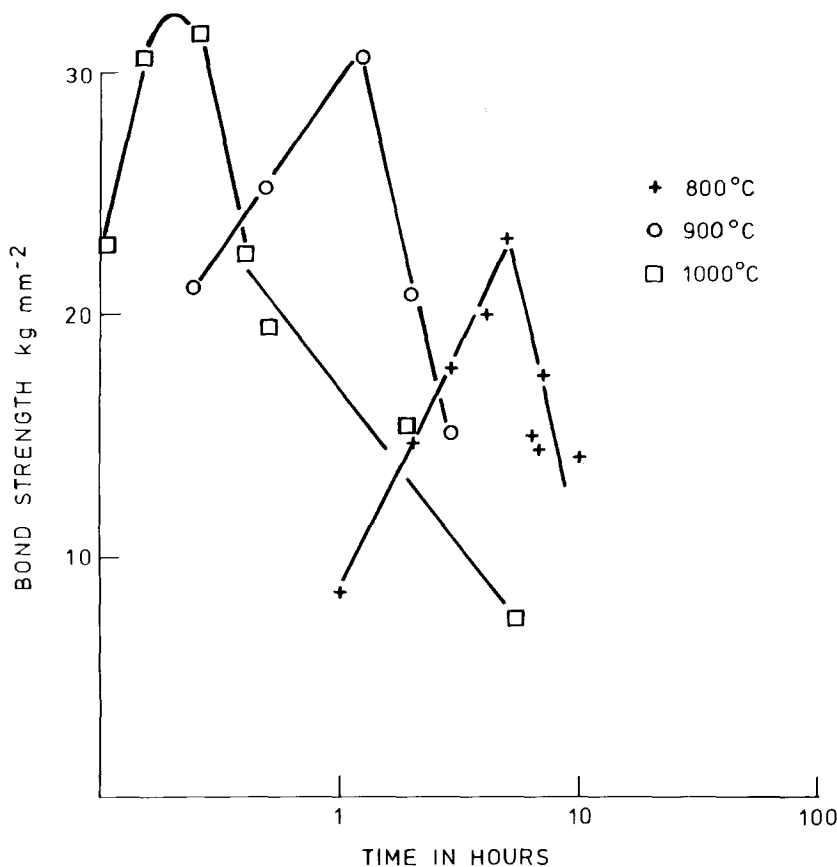
Figure 3 The effects of fabrication time and temperature on the bonding of a copper–0.09% boron alloy to diamonds.

24.2, 21.4 and 23.5 kg mm^{-2} for copper–0.73% titanium, copper–0.27% chormium and copper–0.09% boron respectively, were lower than the best results obtained in the liquid-phase bonding studies, but their reproducibility was much better. The temperature dependence of the optimum hot-pressing time for the copper–boron alloy was determined by measuring the bond strengths of samples produced at 900 and 1000° C as well as the normal 800° C. As Fig. 3 shows, the optimum bonding time decreased by a factor of 20 as the fabrication temperature was raised from 800 to 1000° C. The maximum strengths of samples pressed at 900 and 1000° C were similar but that of those pressed at 800° C was lower.
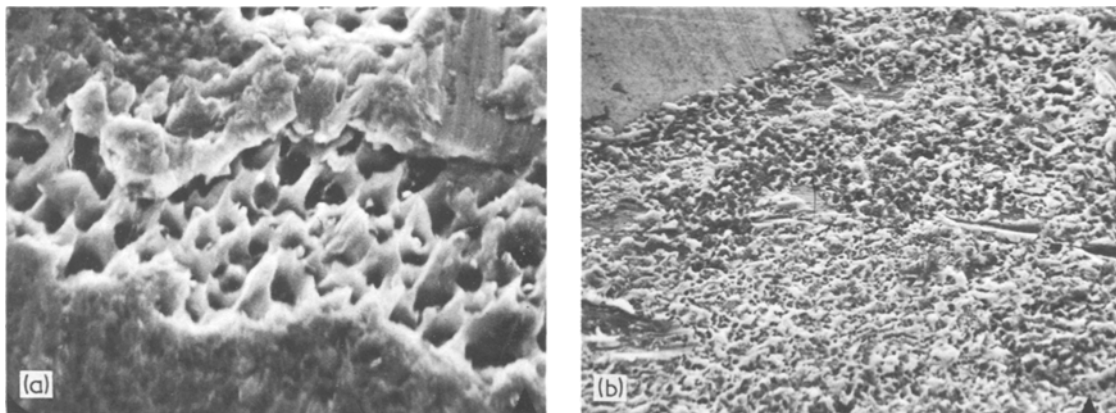
The diamond fracture surfaces were examined

Figure 4 Scanning electron micrographs of the fracture surfaces of diamonds that had been hot-pressed against (a) nickel for 5.0 h, and (b) nickel–1.24% titanium for 0.5 h, × 1600.

using both optical and scanning electron microscopy. The surfaces of diamonds that had been bonded to pure copper were clean but all the others had material still attached that had separated from the cylinders in a ductile manner as illustrated by the micrographs in Fig. 4. Diamonds that had been hot-pressed against the cylinders for less than the optimum time invariably had patches rather than a complete layer of metal retained on their fracture surface. The patches seemed to be randomly distributed in the case of diamonds that had been bonded to copper alloys but were in the form of concentric rings on surfaces separated from nickel or nickel alloys, presumably related to the original machined surfaces. Representative micrographs showing the nature of the patchiness and its replacement by a uniform or near uniform layer on diamonds hot-pressed for longer times are presented in Fig. 5.

The surveys made using the Talystep instrument showed that the diamond—copper alloy fracture surfaces were above or at the level of the surrounding diamond and that diamond—nickel and diamond—nickel alloy fracture surfaces were sometimes above and sometimes below that level. After removal of residual metal and carbide reaction products by chemical cleaning, the diamond surfaces were resurveyed for evidence of erosion produced by contact with the metals and alloys. It was no longer possible to define visually the copper alloy—diamond contact areas and "blind" surveys failed to reveal any feature deeper than $100 Å$, little more than the height of some cleavage steps present on the diamond surfaces. Unmistakable erosion pits were present on diamond surfaces that had been in contact with nickel or nickel alloys. Their depths varied by about an order of magnitude as the fabrication time increased a hundredfold, but there was no significant effect of the presence of carbide-forming elements as shown in Fig. 6.

The fracture surfaces of the detached metal cylinders and polished cross-sections of cylinders were examined using optical microscopy. There was evidence of deformation associated with the fracture surface but no reaction product carbide
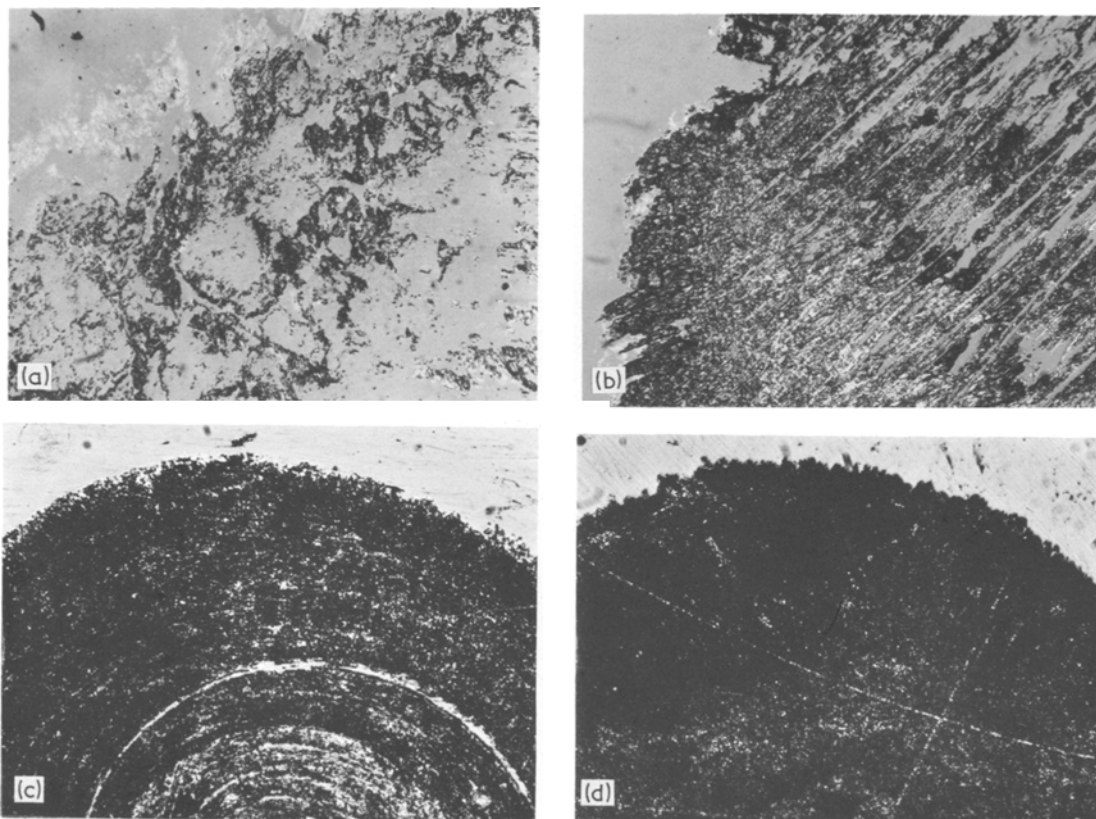

Figure 5 Optical micrographs of the fracture surfaces of diamonds that had been hot-pressed against copper—0.55% titanium for (a) 1.1 h and (b) 2.0 h or nickel—1.24% titanium for (c) 0.2 h or (d) 5 h, × 61.
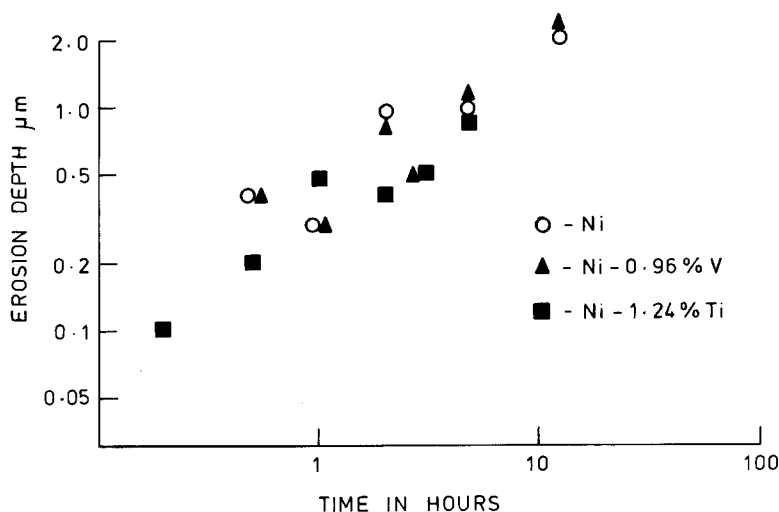
Figure 6 The effects of alloying additions and contact time on the erosion of diamonds by nickel at 800° C.

layers or patches were observed.

The effects of fabrication variables on the abrasiveness of the few diamond grit metal disc samples produced in this programme are summarized in Table I. Increasing the hot-pressing time used to fabricate the copper—0.66% titanium compacts improved their abrasiveness and any

TABLE I Summary of grinding test results

Alloy	Fabrication conditions		Grinding ratio
	Temperature (°C)	Time (h)	
Cu–0.13% Cr	800	1	22.2
Cu–0.13% Cr	700	5	23.5
Cu–0.66% Ti	700	1	22.0
Cu–0.66% Ti	700	5	40.1

Figure 7 Scanning electron micrograph of the surface of a diamond grit copper—0.73% titanium alloy compact, produced by hot-pressing for 5.0h at 700° C, used to abrade steel sheet for 0.5h, 60° C, × 120.

possible detrimental effect of reducing the fabrication temperature of copper—0.13% chromium compacts was offset by the use of an increased fabrication time.

Examination of the grit-disc surfaces before and after the samples had been used in the abrasion tests revealed signs of metal erosion but little damage to the grit as illustrated by the micrograph shown in Fig. 7.

4. Discussion
The experiments described in the previous section have confirmed and greatly extended the results of Schmidt—Brücken and Schlapp [3] demonstrating beyond doubt that alloying with carbide-forming elements can markedly improve the solid-phase bonding between diamonds and copper provided that the fabrication conditions are carefully controlled. Beneficial effects of alloying on diamond nickel bonding are less apparent, but there does appear to be some small improvement in the strengths of samples bonded for less than the optimum fabrication time. Thus the experimental results have revealed a significant difference in the effect of alloying on the two solvent metals employed.

The beneficial effects of alloying on bonding between diamonds and copper provides support for the actual or implied claims of many patents describing solid-phase processes for producing metal matrix diamond grit compacts. However, the mechanism by which the presence of the carbide-forming elements enhances bonding is not entirely clear and seems to be complex. Thus the

1088

degree of improvement depended critically upon the duration of the bonding process, and the optimum fabrication times were temperature dependent at least in the case of the copper—boron alloy/diamond samples. Presumably the improvement is associated with the formation of carbides at the metal/diamond interfaces as was the case with liquid-phase bonded samples, and this is consistent with the discolouration of the alloy interfaces which became more marked with increasing fabrication time although no direct chemical evidence of carbide formation was obtained in this work.

It was suggested in a previous paper that bonding between diamonds and molten copper alloys was promoted by the nucleation of islands of carbides that were chemically linked to both diamond and alloy, and that the strongest bonding was associated with joining of separately nucleated islands to form a complete interfacial layer. Experimental measurements of the degree of diamond erosion suggested that this joining occurred when the average thickness of the reacted layer was about 1000Å, for liquid-phase bonded samples. In the present work it has been concluded that the erosion of diamonds, and hence the carbide thickness, in contact with copper alloys for several hours at 800°C was no more than 100Å. If the solid- and liquid-phase bonding mechanisms are identical, this difference in erosion suggests that many more interfacial carbide nucleation sites are available at 800 than at 1150°C and that, therefore, the islands are, on average, thinner when they first join to form a continuous layer. It has not been established which of the steps involved in the formation of an interfacial layer, such as the arrival of carbon and carbide-forming metal at a nucleation site, nucleation or the growth of nuclei, is dominant. However, the temperature dependence of the optimum fabrication times for copper—boron/diamond samples, shown in Fig. 3, is equivalent to $41 \, kcal \, g^{-1} \, mol^{-1}$, and it is interesting to note that this large apparent activation energy falls within the range of 40 to 56 kcal $g^{-1} \, mol^{-1}$ reported for the volume diffusion of many alloying elements in copper [6].

The strengths of nickel and nickel alloy samples when plotted against fabrication time displays maxima similar to those of copper alloy samples but it is not easy to interpret these results in terms of a possible bonding mechanism. Thus, even though the Talystep surveys revealed considerable erosion of the diamonds, there is no direct evidence of the formation of carbide layers. While several mechanisms can be suggested that could account for the observed strengthening effects, it is also possible to rationalize the bond strength data in terms of the island model since it is not necessary for thick carbide layers to be formed. The strength maximum displayed by the nickel samples could be due to the trace impurities present in the spectroscopically pure metal such as silicon, or possibly to the formation of Ni_3C. Although the differences are relatively small, the greater strengths achieved by dilute alloy samples hot-pressed for the optimum, or less than the optimum, fabrication times are consistent with the carbide island model.

Whatever the mechanism, the present work has demonstrated that the strengths of solid-phase bonds produced between copper and diamonds can be considerably improved by alloying with carbide forming elements and carefully controlling of the fabrication conditions. Even when a metal which interacts with carbon is used (nickel), the strengths of bonds formed by hot-pressing markedly depend on fabrication conditions and can be slightly enhanced by alloying with strong carbide-forming elements. These conclusions can have considerable technical importance when interfacial bonding significantly affects metal—diamond component performance. The few results obtained in this programme on the effects of fabrication conditions on the abrasiveness of diamond grit/copper alloy compacts illustrate the benefits that can be obtained. Elsewhere [7] we have disclosed that the wear rate of resin-bonded abrasive grinding wheels can be reduced by replacing conventional nickel-coated diamond grit with heat-treated nickel—titanium alloy coated grit. No doubt other examples can be cited by readers who are familiar with diamond fabrication processes.

Acknowledgements

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