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On brazing of cubic boron nitride abrasive crystals to steel substrate with alloys containing Cr or Ti

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An investigation has been carried out to gain information about the capabilities of some filler alloys for direct brazing of CBN (cubic boron nitride) grits to a steel substrate. It has been found that a Ni–Cr alloy, known for effective diamond brazing, failed to show satisfactory wetting and bonding characteristics towards CBN under the same brazing conditions as that of diamond. The situation could not be improved either by increasing the wt% of Cr or the brazing temperature. Also, prolongation of the brazing time did not show any significant change. It was further revealed that a Ag–Cu–Ti alloy, which is well established for the brazing of diamond and ceramics, exhibited good wetting and bonding towards CBN at moderate temperature. Based on the thermodynamic properties of various materials, characteristic properties of elements of group IV B to VI B and the physical observations made during the investigation, it is suggested that the transition elements of group IV B, such as Ti or Zr, are preferred to transition elements of group VI B, such as Cr, as an activator to promote the wetting characteristics of the braze alloy towards CBN, which is far more chemically stable than diamond.

1. Introduction

In recent years, the brazing of diamond grits to a steel substrate in a monolayer configuration with a suitable braze material has gained tremendous importance in industry, with a view to manufacturing tools which can out-perform conventional galvanically bonded diamond tools.

The chemical nature of bonding as obtained during brazing makes possible the use of a lower level of bonding material in comparison to what is required in galvanic bonding, which provides mechanical hold on the grits [1]. This unique characteristic of the brazed bond can be translated into higher material removal rate and longer tool life in comparison to that of a galvanically bonded tool.

The basic requirements of a braze material used for diamond–metal joining are those of any other type of filler metal; that it should be capable of wetting and bonding the diamond.

The good compatibility of Ni–Cr alloys has already been utilized to fabricate abrasive tools with tungsten carbide particles by liquid phase bonding [2–6]. The other constituents of these alloys are Fe and B. Sometimes Si and Mo are also present. The use of Ni–Cr alloys containing Si or Si and Ti in brazing graphite to steel has also been reported [7].

Binary alloys such as Cu–Ti, Sn–Ti and Cu–Cr can wet diamond [8] at rather high temperatures. Instead of binary alloys, the use of ternary alloys such as Cu–Sn–Ti [9–11] or Cu–Ag–Ti [12] is also well established. Cu–Ga–Cr alloy is also known to wet diamond effectively at a moderate temperature [13]. Ag–Mn–Zr alloys with a high percentage of silver can be used for brazing diamond grits to a metal support [14].

Although Cu or Ag based active brazing alloys are quite capable of direct brazing of the diamond tool tip (used for turning), structural ceramic and graphite, it is contended [15] that these alloys are of low strength and wear resistance and are not suitable, as the bonding matrix to fabricate monolayer diamond abrasive tools. The matrix, holding the abrasive grits, should be strong and should not yield under the action of the cutting force transmitted to it by the grit [10, 16]. The brazed bonded single layer diamond abrasive tool, which is reported to out-perform the galvanically bonded counterpart in terms of grit retention and prolonged tool life, could come into being only with the use of Ni–Cr based alloys as the brazing matrices [1, 15]. Though Ni–Cr based alloys are quite effective for direct brazing of diamond, no information is available so far on the behaviour of such alloys towards CBN. Therefore, the basic objective of this study was to investigate the effectiveness of Ni–Cr alloys and to compare the same with that of Ag–Cu–Ti alloys as an active braze to wet and bond CBN grits to a steel substrate.

2. Experimental procedure

In order to make the comparative study meaningful,

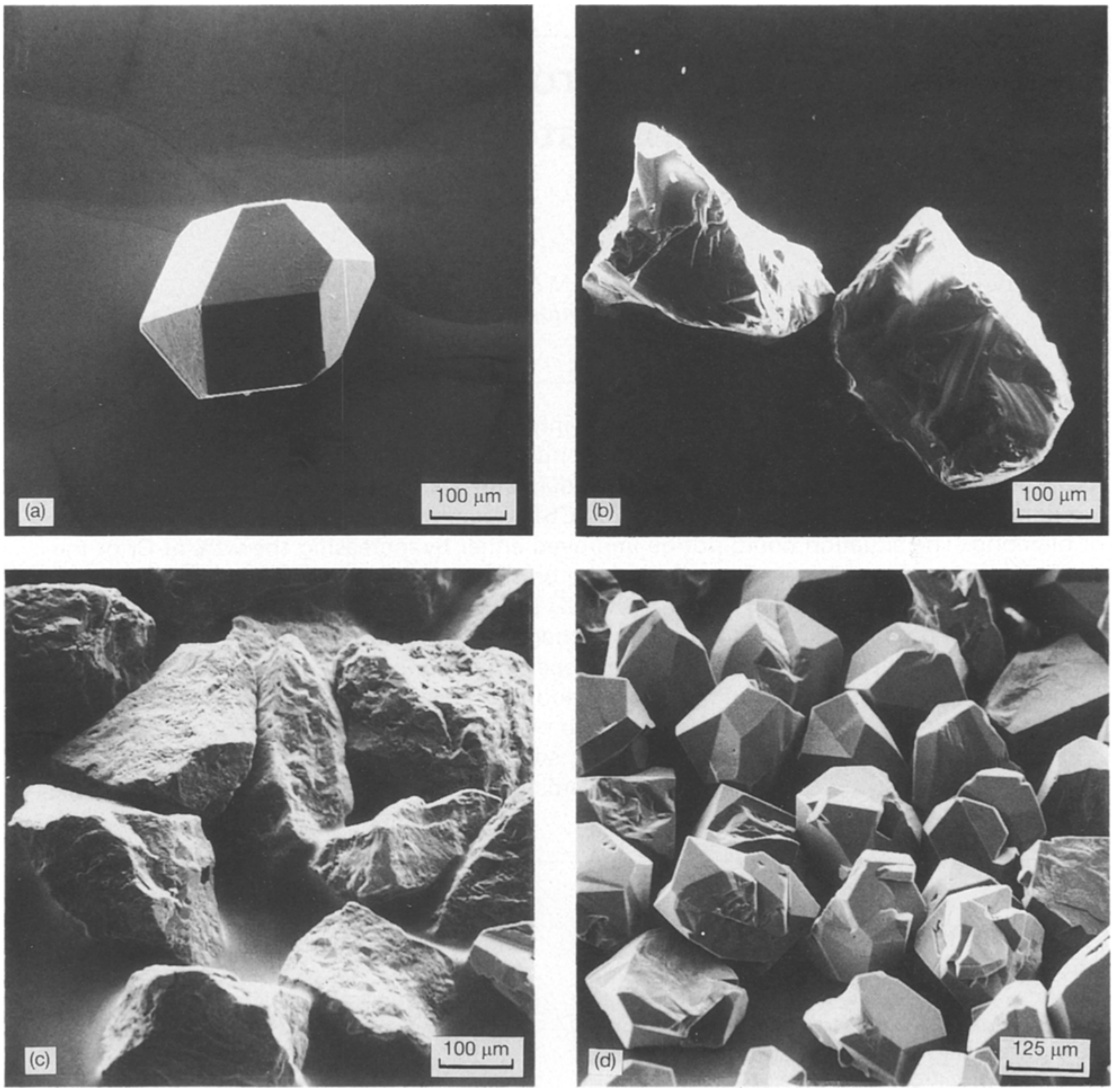

Figure 1 Micrographs showing (a) synthetic diamond, (b) natural diamond, (c) microcrystalline CBN and (d) monocrystalline CBN.

both synthetic and natural diamond grits were included, along with microcrystalline and monocrystalline CBN grits, in the investigation. The four types of grits are shown in Fig. 1. Before being used, all types of grits were degreased by ultrasonic cleaning in parchloroethylene followed by isopropyl alcohol for 5 min each and dried in hot air. No other chemical or thermal treatment was carried out on the grits. The size of the grits was defined by 212–250 µm mesh width.

2.1. Interaction of Ni–Cr alloys with diamond grit

A commercially available Ni–Cr alloy with a composition of 76 % Ni, 14 % Cr and 10 % P was used for brazing purposes. This composition was very close to a composition specified in the patent literature [15]. The said alloy was applied on the top surface of the steel button in the form of a paste, followed by sprinkling of diamond grits onto it. The melting point of the alloy was 890 °C. The brazing was carried out at 1000 °C for 30 s in a dry hydrogen atmosphere.

The micrographs of Fig. 2 reveal that both natural and synthetic diamond grits were effectively wetted under the brazing conditions and the molten alloy could reach the top of the grits, indicating spontaneous wetting. This observation undoubtedly justifies the claim made in the patent [15].

2.2. Interaction of Ni–Cr alloy with CBN grit

Attempts were made to braze microcrystalline CBN grits with the same brazing alloy under the same brazing conditions as described under section 2.1, but without success. When no visible wetting of CBN was possible at 1000 °C, the temperature was raised to 1050 °C, keeping the time at temperature only 30 s. Fig. 3(a) shows that by raising the brazing temperature, no improvement in wetting could be achieved. Elevating the temperature as high as 1100 °C and extending the time at temperature to 10 min did not

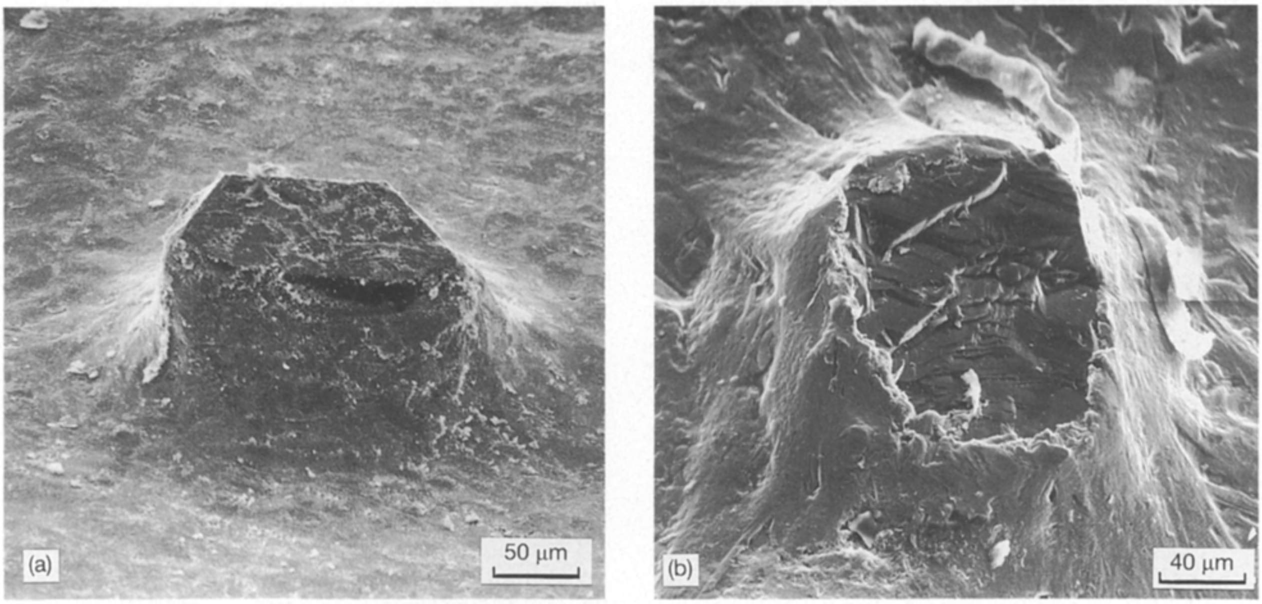

Figure 2 Wetting and bonding of (a) synthetic diamond and (b) natural diamond grit by a Ni–Cr alloy containing 14% Cr during brazing at 1000 °C for 30 s under a dry hydrogen atmosphere.

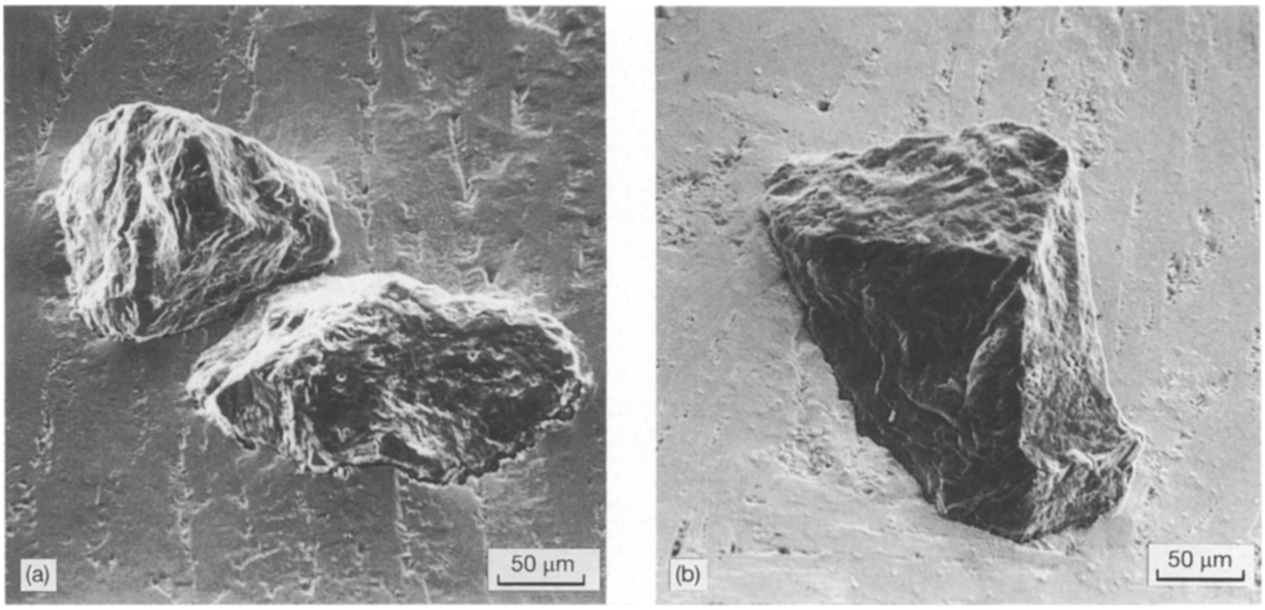

Figure 3 Appearance of microcrystalline CBN grit buttons after brazing under a dry hydrogen atmosphere with a Ni–Cr alloy containing 14% Cr (a) at 1050 °C for 30 s and (b) at 1100 °C for 10 min.

make any significant change in the wetting behaviour of the alloy, as is evident from Fig. 3(b).

It is further revealed in Fig. 4 that a Ni–Cr alloy with higher chromium content (25 % Cr, 65% Ni and 10 % P) than the former did not promote wettability of the alloy towards CBN either. The solidus and liquidus points of this alloy were 880 °C and 950 °C, respectively. Brazing was carried out at 1100 °C for 10 min under a hydrogen atmosphere.

It was interesting to note that the interface between the CBN grits and the metal matrix shown in Fig. 4 was of inadequate strength and that the abrasive grits could be plucked rather easily by pushing with a hardmetal pencil or by pulling with resinoid tape. In most cases, the pockets thus formed were seen to have featureless surfaces, as illustrated in Fig. 5, suggesting the absence of chemical adhesion.

Figure 6 visualizes the appearance of a grit surface which formed an interface with the bonding matrix and later pulled out. The surface feature does not give any positive impression of reaction with the bonding matrix. Elemental analysis carried out on different points on the surface of the CBN grits shown in Fig. 6 and displayed in Table I hardly confirms the existence of Cr or Ni. This observation suggests poor reactivity of the braze alloy towards CBN.

Neither of the Ni–Cr brazing alloys showed any sign of promise in wetting monocrystalline CBN grits. Fig. 7 confirms that the alloy with 25 % Cr proved to be ineffective in wetting and bonding when the brazing

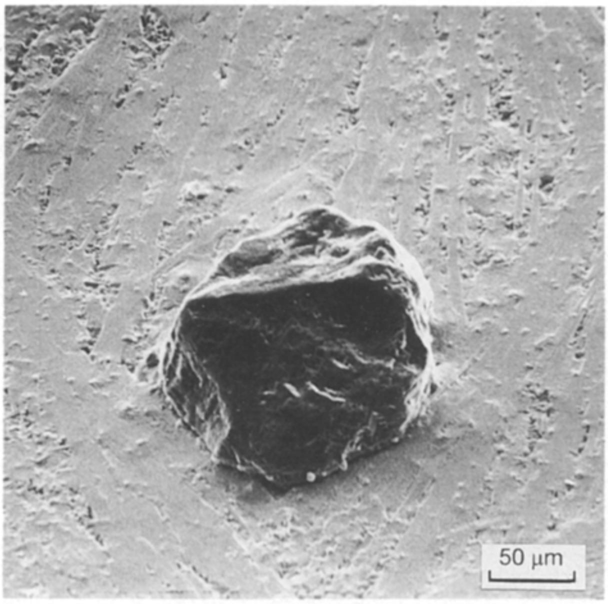

Figure 4 Appearance of microcrystalline CBN grit buttons after brazing with a Ni based alloy containing 25%, Cr under a dry hydrogen atmosphere at 1100 °C for 10 min.

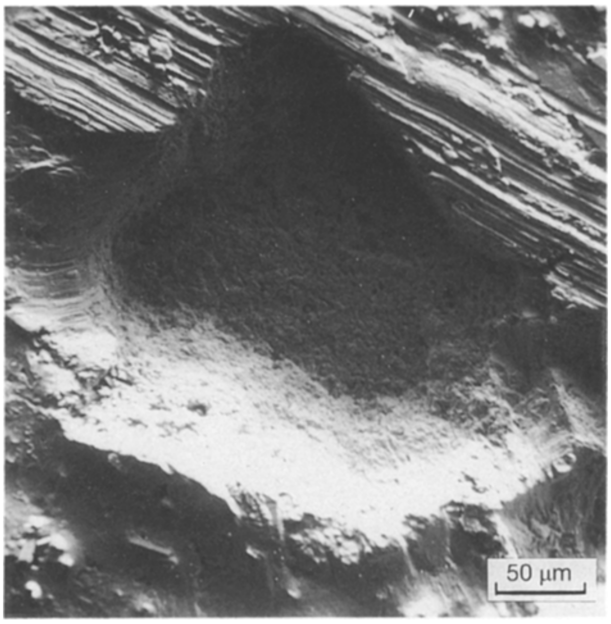

Figure 5 Micrographs showing the hole formed upon dislodgement of a CBN grit from the matrix.

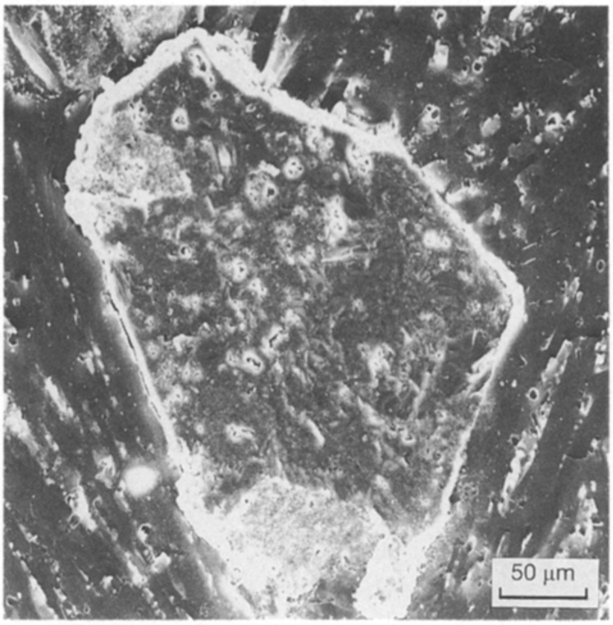

Figure 6 Micrographs showing CBN grit surface in contact with the metal matrix upon separation from it.

TABLE I Analysis of elements (wt %) at different points on the surface of the CBN grits of Fig. 6

B	N	Cr	Ni
35.9	57.8	0.3	1.9
38.2	55.7	0.1	0.8
40.2	53.8	0.2	1.4
36.7	58.1	0.1	1.0
32.3	60.5	0.4	2.8

temperature was maintained at 1100 °C for 10 min. This was in contrast to effective wetting of synthetic diamond with a smooth surface even at a lower temperature, as demonstrated in Fig. 2(a).

As expected, Fig. 7 also shows that monocrystalline CBN grits could easily be removed from the matrix. The pockets thus formed after removal of the grits also appeared to be featureless. Hardly any broken-off fragments of the crystals could be recognized in the matrix.

2.3. Interaction of Ag–Cu–Ti alloy with CBN grit

Ag–Cu–Ti alloys with varying Ti contents are available commercially. Such an alloy with a composition of 72 % Ag, 20 % Cu and 8 % Ti was applied on the surface of a steel button, followed by the sprinkling of CBN grits onto it. The melting point of the alloy was 780 °C. Brazing was carried out at 900 °C for 30 s under an argon atmosphere. It can be seen from Fig. 8 that smooth surfaces of monocrystalline grits were satisfactorily wetted by the alloy, in contrast to the non-wetting character of Ni–Cr alloys even at temperatures as high as 1100 °C. Wetting of bulk hexagonal BN with Ag–Cu–Ti alloys containing 70 % Ag, 28 % Cu and 2 % Ti at 950 °C has also been reported [17].

EPMA surveys across the braze–CBN interface are shown by the traces in Fig. 9. The main information which could be derived was the preferential segregation of Ti towards the interface. A gradual fall in the concentration of copper towards the interface also confirmed this.

The brazed CBN abrasive button was made to abrade against a disc of 100 Cr 6 steel at a speed of 30 m s^{-1} with a normal load of 20 N for 15 min. The preliminary observation made in Fig. 10 suggests that there was no grit pull out. The same figure further revealed that the CBN crystals fractured to different degrees during the course of abrasion. However, it was felt that actual grinding tests with brazed CBN tools having standard shapes should be carried out to obtain needed information about the reliability of such soft alloys in holding the CBN grits.

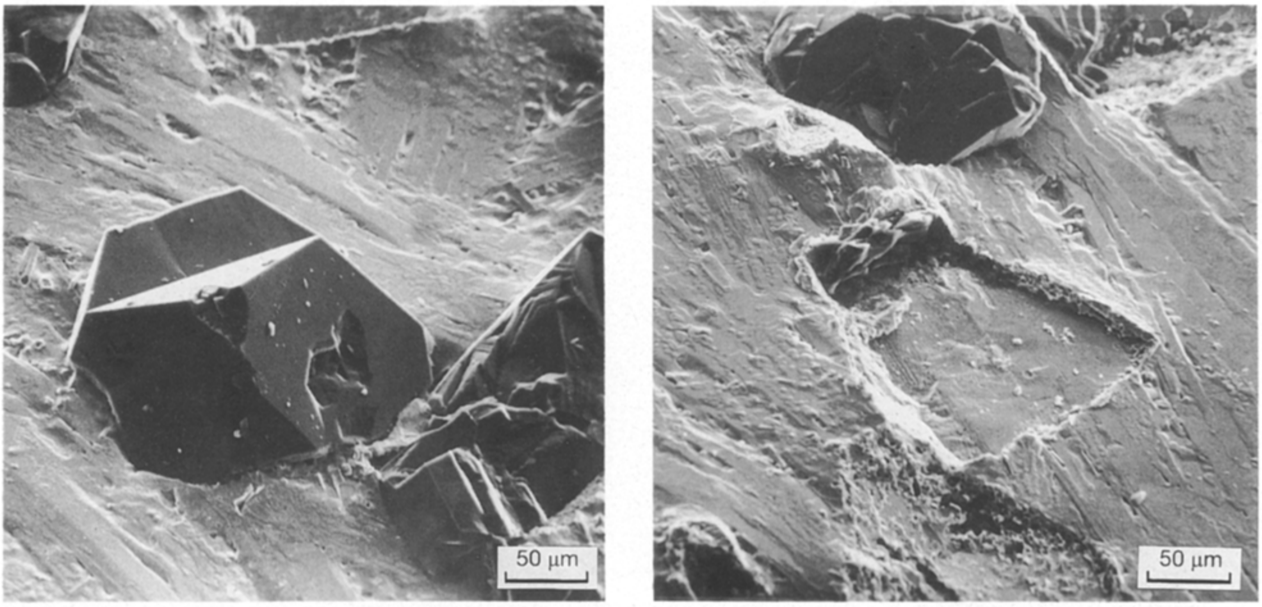

Figure 7 Micrographs showing poor wetting and bonding of monocrystalline CBN grits with a Ni–Cr alloy.

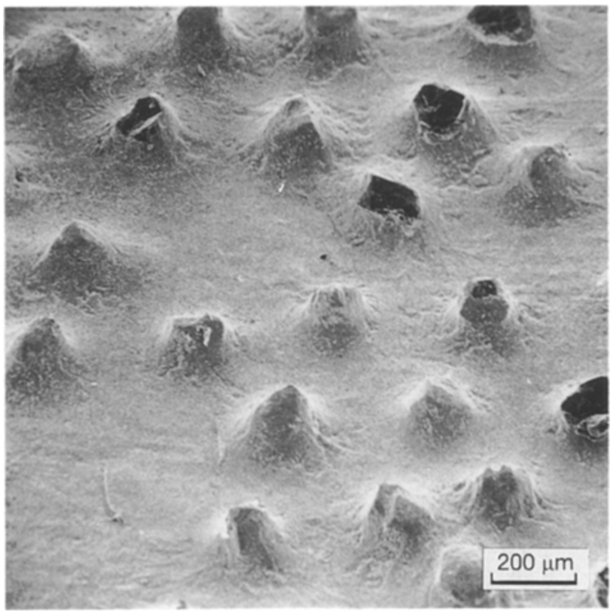

Figure 8 Wetting of monocrystalline CBN grits with Cu–Ag alloys containing 8% Ti at 900 °C.

TABLE II Number of d-shell electrons of transition elements

	Group		
Period	IV B	V B	VI B
	Ti	V	Cr
4	2	3	5
	Zr	Nb	Mo
5	2	4	5
	Hf	Ta	W
6	2	3	4

TABLE III Free energy of formation and heat of formation of different materials at 298 K

	Free energy of formation (kcal mol^{-1})	Heat of formation (kcal mol^{-1})
Diamond	0.6850	0.4532
BN	– 53.783	– 59.970
Cr_3C_2	– 19.5	– 19.3
Cr_7C_3	– 39.9	– 38.7
$Cr_{23}C_6$	– 89.3	– 87.2
CrN		– 29.8
Cr_2N		– 30.5
TiC	– 43.2	– 44.1
TiN	– 73.48	– 80.70
TiB	– 38.171	– 38.300
TiB_2	– 76.4	– 77.4
ZrC	– 47.7	– 48.5
ZrN	– 80.47	– 87.300
ZrB	– 76.789	– 77.100

3. Discussion

The principle of direct brazing of a ceramic with an active alloy is that the transition element (with an unfilled d electron shell), present in the brazing alloy should react with the ceramic surface, thus forming a metal rich reaction product which possesses good metallurgical compatibility with the alloy. In this respect, the chemical stability of the ceramic plays a dominant role. The degree of reactivity of the transition element also depends on the number of d-shell electrons and the prevalent temperature [18]. Table II shows that transition elements of group IV B has less d-shell electrons than those of group VI B. Based on the thermodynamic data presented in Table III, it can be concluded that both Cr and Ti can react with diamond because of the higher chemical stability of their carbides than that of diamond. The strong reactivity of Cr towards diamond during brazing in a marginal atmosphere has already been demonstrated [19, 20].

To be able to react with CBN, it is essential that the elements under consideration should form a stable nitride or boride. Generally, nitrides are more stable than corresponding borides. Stable nitrides are formed either by silicon or gallium [8]. However, their heat

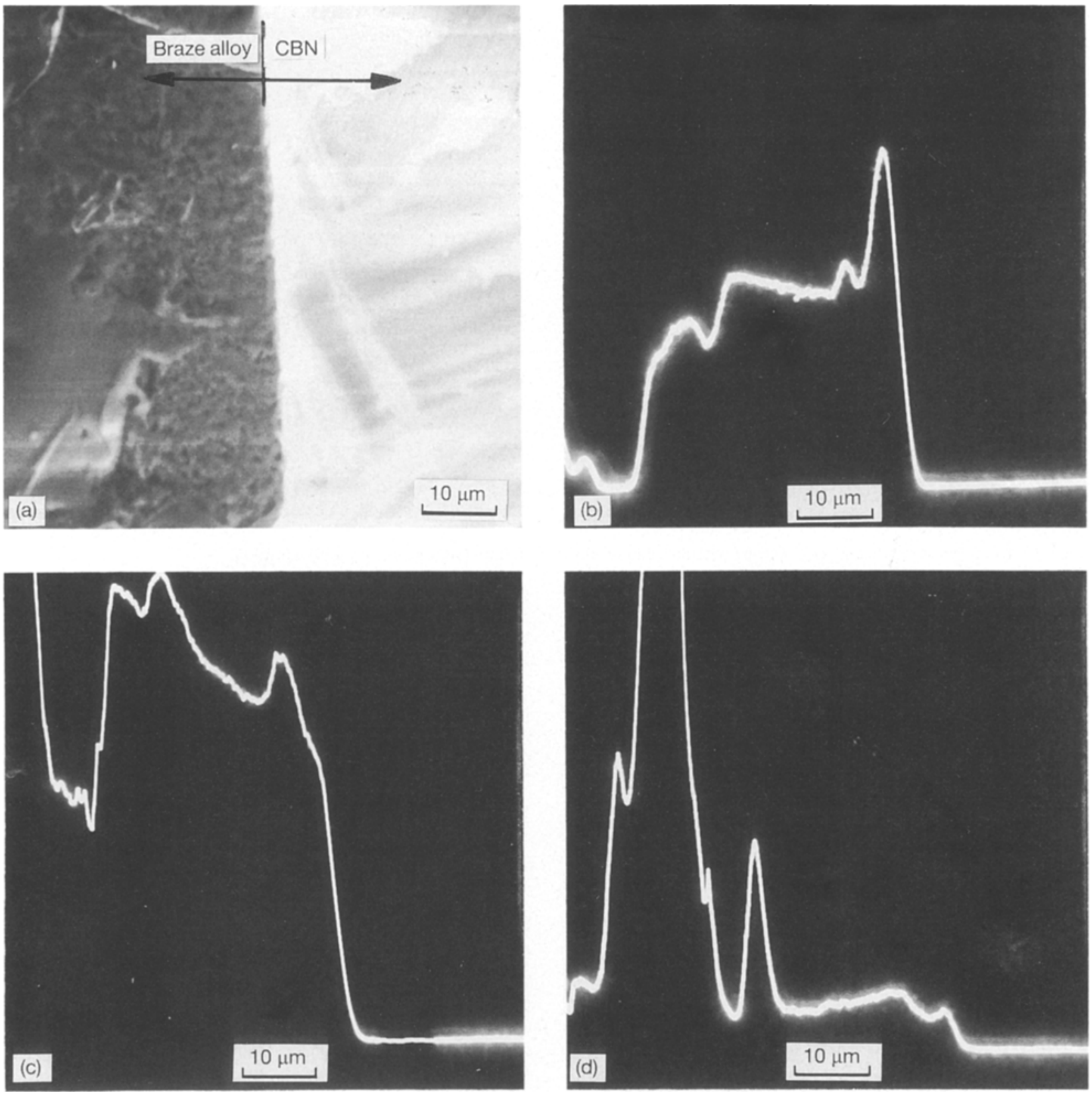

Figure 9 Micrographs showing (a) interface between Ag–Cu–Ti braze and CBN and EPMA traces of (b) titanium, (c) copper and (d) silver across the interface.

of formations (− 45 and − 25 kcal mol^{-1}, respectively) are much less than that of boron nitride (− 60 kcal mol^{-1}) [8]. Silicon makes a high contact angle, 95° at 1500 °C with CBN because of non-reactivity. On the other hand, Al can form AlN, which has a greater heat of formation than BN. The contact angle of liquid Al on CBN is 60° at 1100 °C [8], which is still high.

To be able to become an active braze alloy, Cr containing alloys should make a stable, well adherent and wettable reaction product at the interface with CBN. A literature search suggests that Cr can be transformed into Cr_2N in a nitrogen atmosphere under a suitable pressure and temperature combination [21]. A Cr film deposited on a steel substrate could also be nitrided through diffusion of nitrogen present in the steel substrate [22]. However, the thermodynamic data for different materials presented in Table III show that the heat of formation of Cr_2N or CrN is far less than that of BN. Similarly, referring to Table IV, it cannot be justified that the strength of the Cr–N bond will be greater than that of B–N. Poor adhesion and inferior wetting because of poor reactivity of Cr towards CBN under the brazing conditions, as observed during the present investigation, can be supported by these data.

It needs further investigation to find out whether the addition of an element or elements to the Ni–Cr braze alloy can increase the activity of Cr and therefore promote its ability to form a stable and wettable reaction product on a CBN surface. Such benefit has already been obtained in Cu–Ti and Cu–Cr systems [13].

It can be recognized from Table III that transitional elements of group IV B, such as Ti, Zr and Hf, form nitrides or borides with higher heat of formation than that of BN and they can form reaction products wettable by the braze alloy. This could be the most

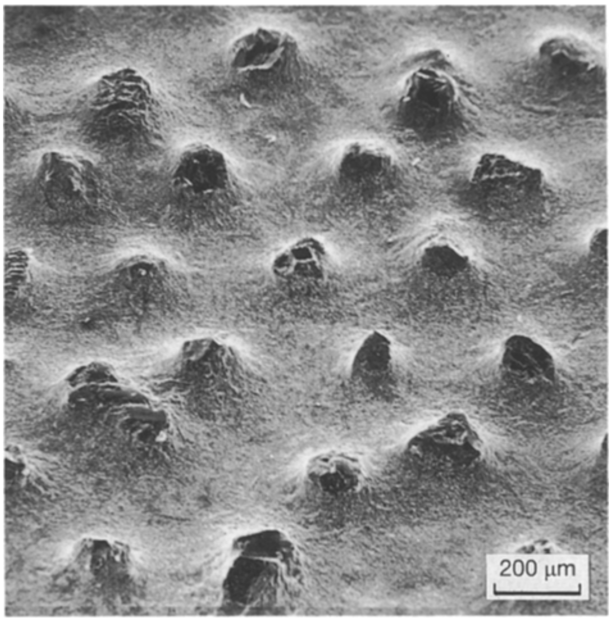

Figure 10 Appearance of monocrystalline CBN grit button fabricated with Ag–Cu–Ti alloys after 15 min of grinding.

TABLE IV Bond strengths

Molecule	Bond strength (kcal mol^{-1})
C–C(diamond)	85.5
B–N	93 ± 5
C–Ti	104 ± 6
N–Ti	111
B–Ti	66 ± 15
Ti–Ti	33.8 ± 5
C–Zr	134 ± 6
N–Zr	135 ± 6
N–Cr	90.3 ± 4.5
Cr–Cr	37 ± 5

reasonable explanation of wettability of Ag–Cu–Ti alloys with both microcrystalline and monocrystalline CBN. Good wettability of hexagonal BN compact, as observed [17] with alloys containing Ti, can also be explained by the same reasoning. It is quite obvious that the reaction product should be a Ti-rich nitride to obtain satisfactory wetting [17]. Following the same logic, it is not difficult to understand the effectiveness of alloys containing Ti or Zr and specified in the patent literature [14, 23] for CBN brazing. It is not unreasonable to imagine that Ti or Zr essentially acts as an activator to promote wettability of these alloys towards cubic boron nitride.

4. Conclusions

1. Ni–Cr alloys, which are known to exhibit good wetting characteristics towards diamond at moderate temperature, failed to show similar behaviour towards both microcrystalline and monocrystalline uncoated CBN crystals.

2. Elevating the temperature or increasing the amount of Cr in the alloy did not produce any noticeable improvement in wetting and bonding characteristics. The CBN crystals could easily be dislodged from the matrix.

3. This can be explained by poor reactivity of Cr with CBN under the brazing conditions to make a well adherent and wettable reaction product on CBN surfaces, as supported by SEM and EPMA studies.

4. Thermodynamic data suggest that Cr can make reaction products rather more easily with diamond than with CBN.

5. Ag–Cu–Ti alloys, which are well known for direct brazing of diamond or ceramics, can also be used for brazing of CBN crystals to a metal substrate. Simulated grinding tests revealed that the grits were retained in the matrix during grinding.

6. This can be explained by the ability of Ti to react with CBN, thus changing its surface chemistry so that wettability of the Ag–Cu system was achieved.

7. Further study is necessary to examine the possible improvement of wettability of Ni–Cr alloys towards CBN through addition of transition elements of group IV B such as Ti or Zr.

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