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Production of copper–matrix composites by *in situ* processing

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Reaction synthesis routes were studied as a means of production of copper–matrix composites. Routes for providing fine and uniform dispersions of TiC, TiB_2 and WC in a copper-rich matrix were identified. The reasons for achieving good dispersions of TiC and TiB_2 in the matrix were explained. The merits of each method were assessed in terms of the potential advantages offered.

1. Introduction

Copper and copper-base alloys have found a wide range of applications where high electrical and thermal conductivities are required. At temperatures in excess of 500 °C, the metal undergoes thermal softening and as a result a substantial deterioration in its tensile strength and creep resistance takes place [1]. Precipitation hardened copper–chromium and copper–zirconium alloys suffer from rapid overageing beyond 500 °C while the higher strength systems based on spinodal alloys are unsuitable for applications demanding a high electrical conductivity. There is clearly a need for copper conductors with electrical conductivity in excess of about 80% IACS (International Annealed Copper Standard) capable of operating above 500 °C for a variety of uses including electrical contacts and resistance welding electrodes. The most likely materials to fulfil such criteria are metal–matrix composites (MMCs) of copper.

Warrier and Rohatgi [2] have shown that TiO_2 dispersions can improve the mechanical properties of copper. Peterson *et al.* [3] demonstrated that a dispersion hardened copper alloy containing 1% ThO_2 by weight retained high electrical and thermal conductivities and possessed mechanical properties which did not exhibit the extreme softening experienced by conventional alloys at elevated temperatures. Al_2O_3 dispersion strengthened copper has been commercially available for a number of years and has found applications at high temperatures. This material is manufactured by the internal oxidation of Cu–Al alloys [4] but the process is inflexible from the point of view of producing bulk structures. It appears that if MMCs based on copper are to gain industrial viability, their processing route must not only optimize the critical properties, but it must also be economical, flexible and reliable. Liquid based routes can provide a means of production with these benefits as well as the ability to form near net shape components by casting. One of the most important recent developments is the Mixalloy process [5] developed at the Massachusetts Institute of Technology (MIT). This process can mix two or more liquid metal streams and generate reinforcement phases by *in situ* reactions. Nanoscale particles (50 nm) of TiB_2 have successfully been generated in copper by such means. MMCs containing 5 vol % TiB_2 have been measured to have an electrical conductivity of 76% IACS.

The purpose of the work reported here was to examine the feasibility of introducing ceramic dispersions into molten copper by *in situ* reactions prior to casting. Such a processing route was successfully used by Terry and Chinyamakobvu [6] to produce iron-based TiC composites. The technique was thought to produce dispersions whose surface may be free from gas contamination and therefore promote the matrix–dispersoid bond.

Three reinforcing materials were chosen for the present study; TiC, TiB_2 and WC all of which were generated *in situ*. TiC was introduced into the matrix by the carburization of copper–titanium alloy melts of appropriate composition using carbon black. TiB_2 was introduced by the carbothermic reduction of B_2O_3 in copper–titanium melts or by the *in situ* reaction between copper–titanium and copper–boron melts. Finally, W and carbon black were reacted in molten copper to produce WC dispersoids. Appropriate measurements were also carried out to investigate the effect of these dispersoids on the electrical conductivity of copper.

In addition to this, a simple dispersion test developed by Terry and Chinyamakobvu [7] was used in the preliminary stages to obtain a qualitative assessment of the dispersion of particles of TiC, TiB_2 and WC in copper. Pellets of the metal containing particles of the ceramic phases were melted and electromagnetically levitated. Samples were quenched and examined microscopically to obtain a visual assessment of the amount of dispersion achieved. In effect, this test provided information on the wettability of the three ceramic materials by copper.

The fundamental theory of the wetting of solids by molten metals has been the subject of a number of recent reviews [8–10]. The wettability of a solid

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reinforcement by a liquid metal is dictated by the strength of the solid/liquid interface as measured by the work of adhesion, W_A. If the surface tension, γ_{LV}, of the liquid metal is known, the work of adhesion can be calculated experimentally by measuring the contact angle, θ, between solid and liquid using the equation [7],

$$W_A = \gamma_{LV}(1 + \cos\theta)$$

The most common method used for assessing the wetting of a solid dispersion by a metal involves the measurement of the contact angle by the sessile drop method. For good wettability, it is essential that the wetting angle is as low as possible, while if θ exceeds 90° the system is said to be non-wetting.

2. Experimental details

All experiments were performed in a special reaction chamber which was filled with static inert argon gas. The raw materials were reacted in graphite crucibles which were heated by means of electromagnetic waves. Cu/TiC composites were produced by reacting Cu/Ti alloys of appropriate composition with carbon black. Cu/TiB_2 composites were prepared by the carbothermic reduction of B_2O_3 in the presence of Cu/Ti alloys of appropriate composition at an argon pressure of 0.507×10^5 Pa to facilitate the evolution of CO and thus avoid excessive porosity in the final products. On completion of the reaction, the chamber was evacuated and re-filled with argon. Cu/TiB_2 composites were also obtained by mixing Cu/Ti and Cu/B melts. *In situ* formation of Cu/WC composites was achieved by reaction of W and carbon black in the presence of molten copper. Following reaction, the products were allowed to slowly cool down in the furnace. The Cu/Ti and Cu/B alloys used in the study had previously been prepared in-house at 1400 and 1600 °C, respectively, using high purity elements. The products were characterized by means of X-ray diffraction (XRD) as well as optical and electron microscopy. Samples for electrical conductivity measurements were rolled into thin sheets using a rolling mill. The electrical conductivity was obtained from resistivity measurements using a 4-point probe system.

3. Results

3.1. Reaction between copper–titanium melts and carbon black

During a preliminary study it was attempted to disperse TiC spherical particles of 20 μm diameter into molten copper by means of injection and levitation. However, both techniques failed as the TiC particles floated on the melt surface achieving no dispersion at all. This result suggested that the wetting of TiC by liquid copper was extremely poor.

When Cu–Ti alloys containing the desired amount of Ti were reacted with carbon black at 1500 °C, the latter was initially observed to rise to the surface of the melt. As reaction with Ti took place, carbon black gradually disappeared from the surface into the melt. The formation of TiC dispersoids in a copper matrix was verified by means of XRD. When carried out in 40 mm diameter graphite crucibles, the reaction between Ti and carbon black to produce 5 wt % TiC in copper took about 40 min for completion. The reaction required much longer to complete when smaller diameter crucibles were used. For example, the reaction was completed in about 3 h when carried out in 15 mm diameter crucibles.

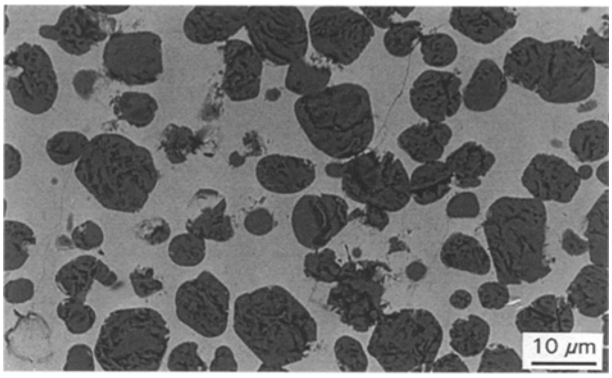

Figure 1 Micrograph of a Cu/55 wt % TiC composite obtained at 1500 °C.

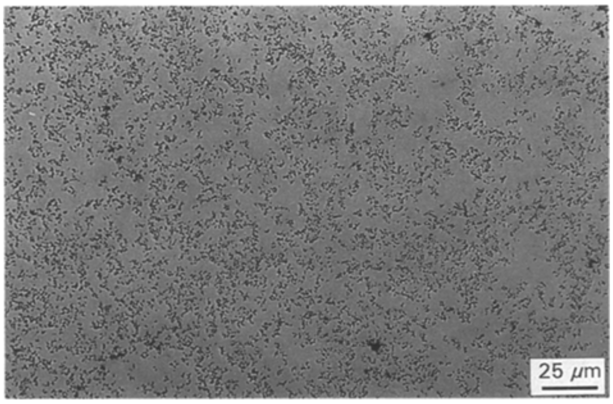

Figure 2 Micrograph of a Cu/5 wt % TiC composite obtained at 1500 °C.

Microstructural observation showed that TiC particles produced by this technique were completely wetted and dispersed in the molten copper. Indeed, dispersions of as high as 55 wt % TiC were achieved as shown in Fig. 1. These dispersoids were relatively large of about 15 μm average diameter. Since several cracks and divisions were present within these particles, it was concluded that they were the result of agglomeration of smaller particles. In comparison, particles in the same sample of a size less than 5 μm in diameter were quite uniform and contained no cracks. A much more desirable particle size was obtained for lower dispersion contents as presented in Fig. 2. This shows fine particles of diameter of about 1 μm for Cu/5 wt % TiC. Using data for the variation of the lattice parameter of TiC with carbon content as presented by Storms [11], the carbide composition ranged from $TiC_{0.83}$ at 1400 °C to $TiC_{0.91}$ at 1500 °C.

As expected, the hardness of these MMCs increased with TiC content as indicated in Fig. 3. However, a significant drop in the electrical conductivity also

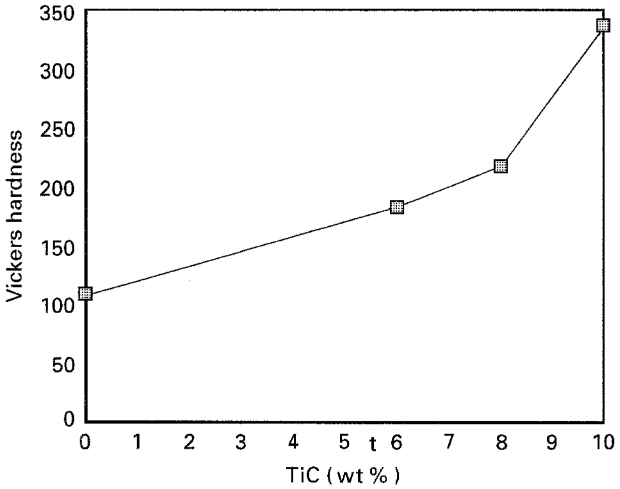

Figure 3 Plot of Vickers hardness (30 kg load) against wt % TiC for Cu/TiC composites.

TABLE I Electrical conductivity measurements (% IACS)

Composite	% IACS
Cu/5% TiC	15
Cu/6% TiC	12
Cu/10% TiC	7
Cu/3% TiB_2	64
Cu/5% WC	92

resulted by generating TiC particles in this fashion, as can be found in Table I.

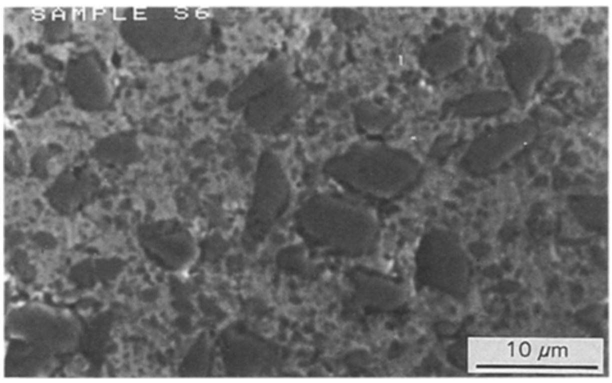

Figure 4 Micrograph of a Cu/18 wt % TiB_2 composite obtained by the carbothermic reduction of B_2O_3 in the presence of a Cu/Ti melt at 1400 °C.

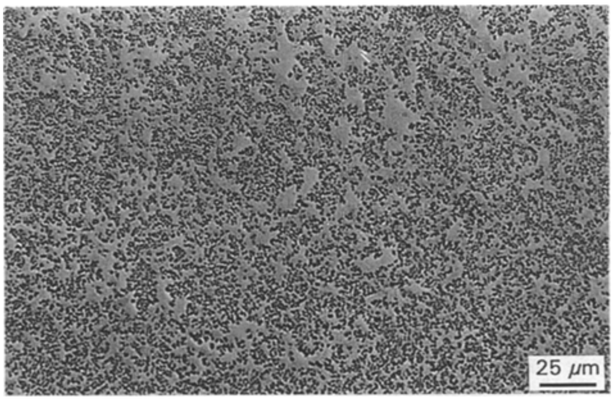

Figure 5 TiB_2 particles in a copper matrix obtained by reaction of Cu/Ti and Cu/B melts.

3.2. Reaction between B_2O_3, carbon black and copper–titanium melts

Preliminary experiments showed hardly any distribution of TiB_2 particles in copper by means of levitation. It was therefore attempted to generate TiB_2 particles in copper by an *in situ* technique where B_2O_3 was carbothermically reduced in copper–titanium melts. This was performed at temperatures of 1400 and 1500 °C and pressures of 0.507×10^5 Pa. A pressure lower than atmospheric was preferred in order to facilitate the evolution of CO produced by the carbothermic reduction and therefore prevent excessive porosity in the product. Of course another effect of the lower pressure was to decrease the temperature at which B_2O_3 could be reduced. While this reaction was taking place, bubbles were observed in the melt thus confirming the evolution of CO. X-ray diffraction data indicated the presence of copper and TiB_2 in the final products. Dispersions of up to 18 wt % TiB_2 were achieved by such means. A typical microstructure for Cu/18 wt % TiB_2 is presented in Fig. 4. Although relatively uniform dispersions of TiB_2 appeared to be achieved, the wetting between the metal and the ceramic was poor. This is much in evidence in Fig. 4 where porous gaps were found surrounding the boride. In spite of the use of low processing pressures, high porosity levels associated with CO gas evolution were obtained. As expected the porosity level tended to decrease as the amount of TiB_2 generated decreased. Thermal conductivity measurements for these composites are presented in Table I and are comparable to those obtained for Cu/TiB_2 composites produced by the Mixalloy process [5].

3.3. Reaction between copper–titanium and copper–boron melts

Copper–titanium and copper–boron alloys of appropriate compositions were placed in a graphite crucible, an ingot of the latter being at the bottom and heated to 1550 °C. Using this arrangement the copper–titanium alloys were gravity-fed into the copper–boron. The original contact area between the two materials measured 7 × 7 mm. A microstructural examination indicated that the two molten alloys mixed only partially at the interface. Analysis of the products showed that only a partial reaction between the two melts took place. The top portion consisted of copper–titanium and the bottom part was copper–boron, while a narrow region of depth of about 5 mm between the two contained TiB_2 in a copper matrix. An example of this is presented in the micrograph in Fig. 5 where a TiB_2 dispersion in copper is shown. Further examination indicated that at the interface of this area, with the two alloys on either side, a continuous TiB_2 layer had formed as shown in the micrograph in Fig. 6. It seemed that this layer prevented further mixing of the two melts and thus prevented further reaction between the two alloys.

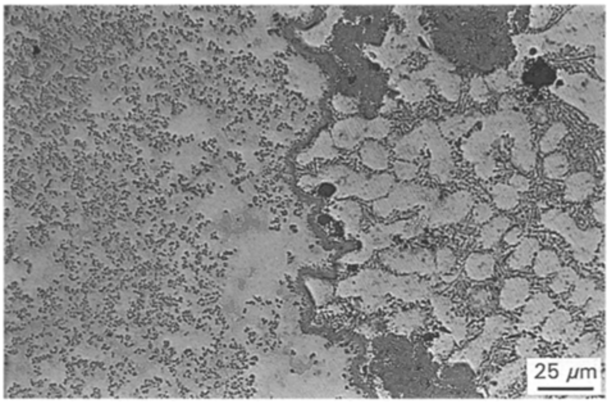

Figure 6 TiB_2 layer at the interface of Cu/Ti with Cu/TiB_2 composite.

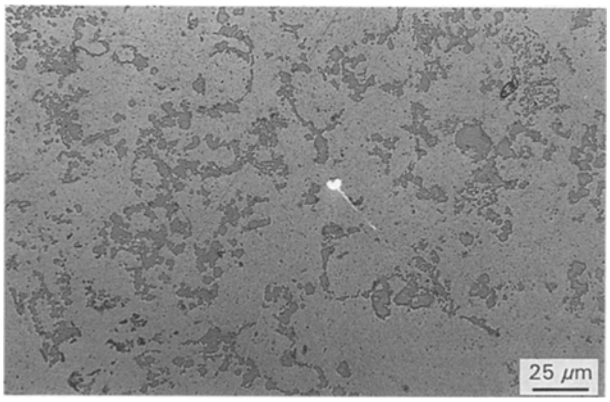

Figure 7 Microstructure of a Cu/5 wt % WC composite produced at 1500 °C. Some particles contain W_2C (light grey) surrounded by WC.

3.4. Reaction between W and carbon black in copper melts

High and uniform dispersions of WC in copper were achieved during preliminary experiments using both levitation and physical injection of the ceramic particles into a copper melt at 1400 °C. *In situ* processing at 1400 and 1500 °C produced fine dispersions of WC of a particle size of 10 μm in a copper matrix. By stopping experiments at appropriate intervals, it was observed that tungsten was initially converted to W_2C and then to WC. The reaction occurred fairly fast and was usually complete after about 15 min. The micrograph in Fig. 7 shows WC particles dispersed in copper. Some of the particles are not fully reacted and contain W_2C which is surrounded by WC. The dispersions achieved soon after completion of the reaction were uniform, but prolonged heating in the melt tended to give rise to segregation in the microstructure. Electron probe microanalysis showed no solid solution of W in the copper matrix.

Electrical conductivity measurements indicated that a Cu/5 wt % WC composite retained a high electrical conductivity of 92% IACS. This figure was similar to the measurements obtained for samples which were produced by the levitation and injection techniques.

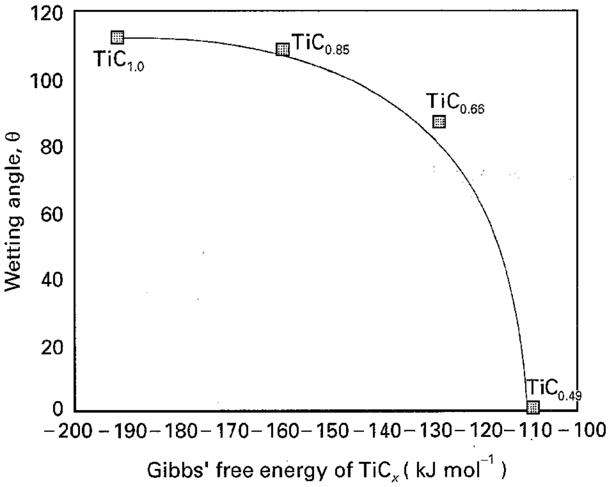

Figure 8 Plot of the wetting angle, θ, between Cu and TiC_x against the Gibbs' Free Energy of formation of $TiC_x(\Delta G^\circ_{f,298K})$.

4. Discussion

4.1. Copper–titanium carbide composites

The failure of the preliminary study to disperse TiC by a levitation technique or by injection of particles into a copper melt was hardly surprising if literature data of the wettability between the two were considered. Wettability depends on the availability of electrons to participate in the bonding between ceramic and metal. Because the electronic structure of copper has a full 3d electron shell, the wettability of the metal for ceramic materials is relatively poor [12]. According to Livey and Murray [13] the wetting angle, θ, between TiC and molten copper at 1200 °C is 95°, while Ramqvist [14] measured an angle of 109°. The latter study, however, showed that θ decreases with the carbon content of the carbide, that is, as the C/Ti ratio in the carbide decreases, the value of θ also decreases. For $TiC_{0.66}$ an angle of 88° was reported, while complete wetting was achieved with $TiC_{0.49}$. This implies that the work of adhesion between Cu and TiC_x increases with decreasing x. The reason for this behaviour is associated with the decrease in the thermodynamic stability of TiC_x as the C/Ti ratio decreases. This relationship can be established by plotting the data obtained by Ramqvist [14] for the wetting angle, θ, between Cu and TiC_x, against data for the Gibbs' free energy of formation of TiC_x [15, 16] as shown in Fig. 8. As the number of vacancies in the carbon lattice increases, the electron concentration in TiC_x also increases and this intensifies the electron transfer between the ceramic and the metal. As a consequence the wettability between TiC_x and copper increases as the value of x in the carbide decreases.

The carbide used for the injection and levitation experiments was $TiC_{0.89}$ and therefore did not wet the copper. On the other hand, the *in situ* reaction of carbon black with Ti in the melt generated titanium carbide which was completely wetted by the copper matrix. The carbide composition obtained ranged from $TiC_{0.83}$ to $TiC_{0.91}$ so a secondary factor may be that the reinforcement which is produced by the *in situ* reaction in the melt, has a surface which is clean and free from gas contamination and therefore the wetting characteristics are altered in such a way as to promote a stronger carbide–matrix bond. The wetting characteristics are further altered by the fact that some Ti remains dissolved in the copper matrix. Unfortunately, no figures are available for the solid solubility of Ti in Cu for the Cu–Ti–C system. The solubility of Ti in Cu for the Cu–Ti system has been measured by Vigdorovich *et al.* [17] to be 7.9 at % at 850 °C and 1.5 at % at 300 °C. Electron probe microanalysis indicated that as a result of the processing there was about 1.5 wt %, that is 2.01 at % Ti dissolved in the matrix. This does not by any means represent the equilibrium value of Ti dissolved in Cu for the Cu–Ti–C system. The reaction between carbon black and titanium in molten copper may be expressed by,

$$[\mathrm{Ti}]_{\mathrm{Cu}} + \mathrm{C} \rightarrow \mathrm{TiC} \qquad (1)$$

and

$$\Delta G = -RT \ln \frac{a_{\mathrm{TiC}}}{a_{[\mathrm{Ti}]_{\mathrm{Cu}}} a_{\mathrm{c}}} = -RT \ln \frac{1}{a_{[\mathrm{Ti}]_{\mathrm{Cu}}}}$$

No thermodynamic data were found for the above reaction in which Ti is not in its pure standard state but is dissolved in Cu. Because copper and titanium form a series of intermetallic compounds it is reasonable to assume that the activity of Ti in copper will show a negative deviation from ideality. The driving force for reaction (1) during the final stages must be extremely low because the activity of titanium is low. Even if treatment was prolonged to establish equilibrium it is quite likely that enough Ti will remain dissolved in copper and will have an adverse effect on the electrical conductivity of the products [18]. The observation that the copper matrix contains about 2 at % Ti helps to explain why the electrical conductivity of the product composites was quite low. It appears that in order to improve the electrical conductivity, a higher carbon activity may be necessary during processing in order to reduce the solubility of Ti in Cu. The production of a thermodynamically more stable reinforcement like $\mathrm{TiB_2}$ may also lead to a decrease in the Ti solid solubility in copper. This is due to B having a greater affinity for Ti than C does.

The following two reaction mechanisms were considered possible:

1. Carbon black initially dissolved in the melt and TiC precipitation took place when the melt became supersaturated with C.
2. Reaction between carbon black and Ti at the melt interface.

When runs were carried out using the same weight of raw materials, but with a different crucible diameter, it was observed that the reaction rate varied as the crucible diameter. Of the two possible reaction mechanisms, only the second one is dependent on the size of the carbon black/melt interface. It was therefore deduced that carbon black and Ti reacted at the melt interface.

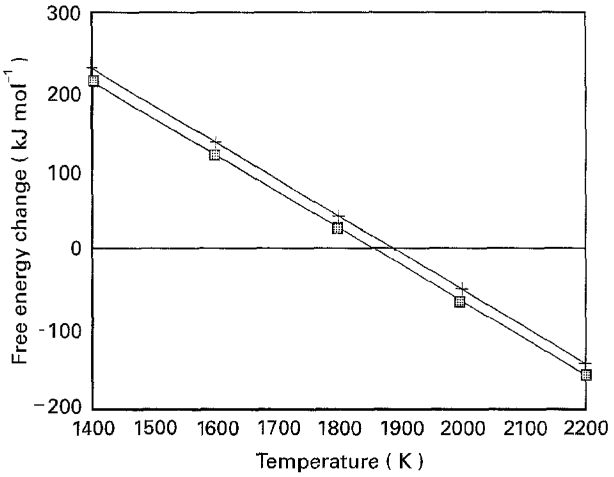

Figure 9 Plot of ΔG° against temperature for the carbothermic reduction of $\mathrm{B_2O_3}$. —▨— Reaction 2 and + reaction 3.

4.2. Cu–TiB$_2$ composites

The most likely reactions which can occur by the carbothermic reduction of $\mathrm{B_2O_3}$ are

$$\mathrm{B_2O_3} + \tfrac{7}{2}\mathrm{C} \rightarrow \tfrac{1}{2}\mathrm{B_4C} + 3\mathrm{CO} \qquad (2)$$

$$\Delta G^\circ = 864\,090 - 464T\ \mathrm{J\,mol^{-1}}$$

and

$$\mathrm{B_2O_3} + 3\mathrm{C} \rightarrow 2\mathrm{B} + 3\mathrm{CO} \qquad (3)$$

$$\Delta G^\circ = 884\,822 - 467T\ \mathrm{J\,mol^{-1}}$$

The thermodynamic data for the reactions at a total of 1.013×10^5 Pa have been plotted in Fig. 9 and show that reaction (2) is the more favourable of the two. Indeed this has been verified by previous work [19]. The overall reaction in the presence of copper–titanium melts can be expressed by

$$[\mathrm{Ti}]_{\mathrm{Cu}} + \mathrm{B_2O_3} + 3\mathrm{C} \rightarrow \mathrm{TiB_2} + 3\mathrm{CO} \qquad (4)$$

XRD analyses of samples obtained at intermediate stages of reaction indicated the presence of Cu, Cu–Ti intermetallics, $\mathrm{TiB_2}$, $\mathrm{B_2O_3}$ and carbon. Neither B nor $\mathrm{B_4C}$ were detected at any stage. Because of this the reaction mechanism could not be substantiated. In the presence of Ti, both B and $\mathrm{B_4C}$ react according to reactions (5) and (6) as shown below to form $\mathrm{TiB_2}$ which is thermodynamically more stable,

$$[\mathrm{Ti}]_{\mathrm{Cu}} + 2\mathrm{B} \rightarrow \mathrm{TiB_2} \qquad (5)$$

$$[\mathrm{Ti}]_{\mathrm{Cu}} + \tfrac{1}{2}\mathrm{B_4C} \rightarrow \mathrm{TiB_2} + \tfrac{1}{2}\mathrm{C} \qquad (6)$$

If the rate of reaction (5) is faster than that of reaction (3) or if the rate of reaction (6) is faster than that of reaction (2), then neither B nor $\mathrm{B_4C}$ are expected to be detected at any stage of reaction. Since B and $\mathrm{B_4C}$ are absent from the XRD data, the above statement is substantiated. Although the dispersion of $\mathrm{TiB_2}$ particles in the matrix appeared to be good and uniform, the wetting was relatively poor. This was due to the evolution of CO gas during the carbothermic reduction of $\mathrm{B_2O_3}$ resulting in a poor bond between the metal and the boride. This problem could have been eliminated if an efficient vacuum system was available to the researchers.

The electrical conductivity measurements for Cu/TiB_2 composites were much higher than those measured for Cu/TiC. Considering these as well as measurements from other workers [5], purely from the point of view of electrical conductivity, if copper–matrix composites are to be produced by reactions of copper–titanium melts, then TiB_2 must be ranked as a more suitable reinforcement material than TiC. This is probably due to the higher thermodynamic stability of TiB_2 (B has a greater affinity for Ti than C does) which is likely to result in a low solid solubility of Ti in Cu.

By mixing copper–titanium and copper–boron melts it was observed that TiB_2 particles could be generated in a copper matrix. However, it proved difficult to achieve a full reaction due to the development of a coherent TiB_2 layer at the interface between the reacting melts. This prevented the two melts to come together to react further.

4.3. Cu/WC composites

Livey and Murray [13] have reported a wetting angle of 7° between copper and WC at 1200 °C, thus indicating a wetting system. WC is thermodynamically less stable than both TiC and TiB_2 so in general it is better wetted by metals. This helps to explain why high and uniform distributions of WC in copper were obtained during the present work. It was very interesting to note that the electrical conductivity measurements for Cu/5 wt % WC composites were high. This suggests that WC is a potential reinforcing material for copper in cases where high electrical conductivity is important. This result was attributed to the fact that tungsten metal has no solid solubility in copper. Overall, *in situ* processing of Cu/WC composites appeared to offer no advantage over the same materials produced by conventional means.

5. Conclusions

The work has shown that *in situ* processing can be used to produce copper–matrix composites incorporating uniform dispersions of reinforcement ceramic phases like TiC and TiB_2 which might otherwise not be wetted by copper. However, electrical conductivity measurements have shown that Cu/TiC composites obtained from such a route are unsuitable for applications where a high electrical conductivity is required. This was attributed to the fact that the matrix retained about 2 at % Ti which had an adverse effect on the electrical conductivity of the product. Cu/TiB_2 composites exhibited a higher electrical conductivity and therefore TiB_2 can be viewed to have a greater potential to be used as a reinforcement material for copper when using a reaction-based route. It is likely that the thermodynamic stability of TiB_2 results in an extremely low content of Ti in the copper matrix. WC appeared to be easily wettable by copper and therefore the reactive processing route would offer no clear advantages over conventional casting techniques.

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