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The wetting and spontaneous infiltration of ceramics by molten copper

A. R. KENNEDY*, J. D. WOOD, B. M. WEAGER
Division of Materials, University of Nottingham, Nottingham, NG7 2RD, UK
E-mail: andrew.kennedy@nottingham.ac.uk

Infiltration trials have been conducted by filling Cu tubes with ceramic powders and melting them under argon. No external forces were applied; successful infiltration of the ceramic relied solely upon favourable metal-ceramic wetting conditions. Oxides and covalently bonded compounds could not be spontaneously infiltrated but transition metal compounds such as NbC, Cr_3C_2, WC, NbB_2 and Cr_2N were. It was impossible to infiltrate any ceramics when oxygen was present in the system. Contact angle data in the literature were found to predict, with fair reliability, infiltration events in Cu-ceramic systems. The good correlation is thought to be due to the ease with which the oxide film can be prevented from forming on molten Cu during both sessile droplet experiments and infiltration processing. *© 2000 Kluwer Academic Publishers*

1. Introduction

High volume fraction metal matrix composites and cermets have been targeted for use in a number of application areas. Most research has been centred about Al alloy matrices but Cu matrix composites also have potential in wear and cutting resistant applications especially if good electrical and thermal conductivity are important. Liquid metal infiltration techniques are the most cost-effective way of producing these ceramic-rich materials and in order to simplify processing, and maximise the strength of bonding between the two phases, it is desirable that the molten metal matrix wets the ceramic reinforcement.

The infiltration of metal into a packed bed of ceramic particles requires tortuous flow of liquid through the interstices. If the particle-liquid interfacial energy is less than the particle-vapour interfacial energy, the work of immersion will be negative and infiltration will not require the application of an external force, i.e. it will be spontaneous [1]. The pressure required for infiltration can also be expressed in terms of the contact angle for a liquid droplet on a solid surface [1, 2] and becomes negative when the contact angle is less than 90°. Contact angles, as determined by the sessile droplet test, are more easily measured than either interfacial energy terms or the work of immersion, but, since the test does not replicate infiltration processing conditions, the applicability of using such data to predict infiltration behaviour has been questioned [3].

Reactive metals, such as Al, will spontaneously incorporate or infiltrate a number of ceramics if wetting between the two phases occurs and if there is no oxide film on the molten metal surface [4]. Because it is difficult to prevent oxide films from forming on reactive metals during sessile droplet experiments [5] and because time dependent, metal-ceramic wetting-enhancing reactions can occur, there is poor correlation between incorporation events and contact angle data [4]. For non-reactive metals that do not form tenacious oxide films, such as Cu, closer correlation between infiltration behaviour and contact angle data is expected. This study aims to determine whether or not spontaneous infiltration of different ceramics by molten Cu can be predicted using contact angle data.

2. Experimental procedure

Infiltration trials were conducted in a very simple manner. Ceramic powders were poured into standard plumbing specification copper tubing, 99.8 wt.% Cu, which was crimped at one end. Pre-preparation of the tube, cleaning with wire wool and brief immersion in a 10% nitric acid solution, was required to remove barriers to wetting such as thick oxide films. During and after filling, the tube was tapped against a solid surface in order to increase the particle packing density to between 50% and 60% of theoretical density. The dimensions of the tube, 15 mm outside diameter, 1 mm wall thickness and 50 mm long, were appropriate to provide sufficient metal to fully infiltrate the interstices in the powder bed. When the tube had been filled, the open end was also crimped shut. The particle sizes for the ceramics studied are given in Table I.

Specimens were placed on porous alumina supports, in a stainless steel boat, and then loaded into a three-zone horizontal tube furnace. The ceramic supports were used to prevent contamination of the copper by the stainless steel boat. Without the supports, the copper

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* Corresponding author.

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TABLE I Infiltration behaviour and its relation to contact angle [5] and heat of formation [6]

Ceramic	Particle size (μm)	Contact angle (°) at temperature (°C)	Infiltration	$\Delta H_{f,298\ K}$ (kJ mol^{-1})
Al_2O_3	<20	155 @ 1100	×	−1684
SiO_2	<5	134 @ 1100	×	−914
B_4C	<25	136 @ 1100	×	−72
Graphite	100 (flakes)	140 @ 1100	×	
SiC	<30	<90 @ 1250	×	−67
TiC	<20	111 @ 1150	×	−185
NbC	<5	70 @ 1150	✓	−139
ZrC	<5	126 @ 1150	×	−202
Cr_3C_2	<20	47 @ 1100	✓	−110
WC	<1	30 @ 1100	✓	−38
TiB_2	<15	142 @ 1120	×	−323
NbB_2	<5	131 @ 1100	✓ (partially)	−252
ZrB_2	<5	42 @ 1100	×	−323
TiN	<10	155 @ 1300	×	−336
NbN	<5	150 @ 1500	×	−235
ZrN	<5	148 @ 1130	×	−370
Cr_2N	<45	36 @ 1130	✓	−115

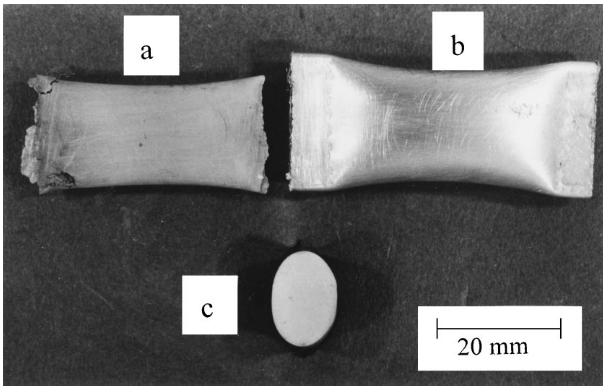

Figure 1 Specimens a) after successful infiltration, b) before heat treatment and c) a cross section through an infiltrated sample.

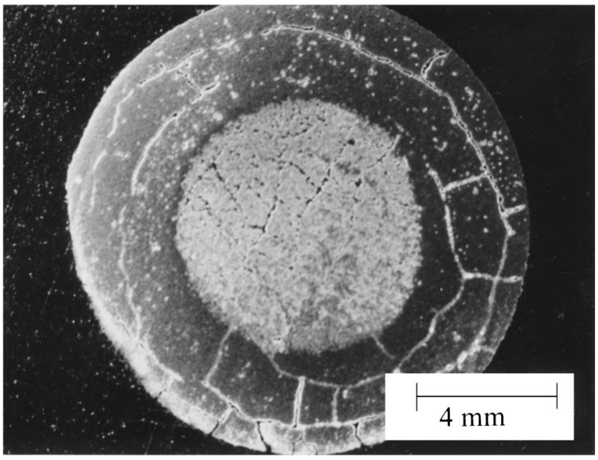

Figure 2 A partially infiltrated Cu-NbB_2 specimen showing cracking in the infiltrated outer region.

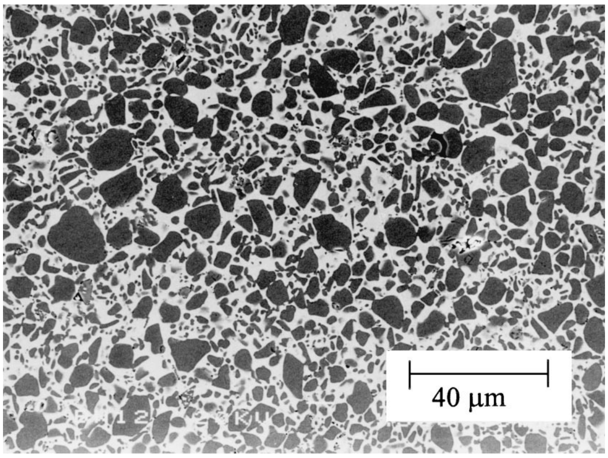

Figure 3 Back-scattered electron image of Cr_3C_2 (dark) spontaneously infiltrated by Cu (light).

was observed to stick to the boat and high levels of Fe, Ni and Cr were detected in the metal.

The furnace was purged with argon gas, of 99.998% purity, for 10 minutes and then heating commenced, at a rate of 30°C min^{-1}, up to 1200°C. The samples were held at this temperature for 30 min before the furnace automatically switched off and cooled to room temperature. It is estimated that the copper was molten for no more than 1 hour. A gentle flow of argon gas was maintained during heating and cooling and a boat containing fine titanium powder was also placed in the furnace to scavenge oxygen and minimise oxidation of both the copper and the ceramic powder.

Samples that had been successfully infiltrated were sectioned, using electro-discharge machining, ground, polished and viewed in a scanning electron microscope (SEM).

3. Results

Table I shows the results of the infiltration trials and compares them with contact angle data, from a review of sessile droplet work by Naidich [5], and heats of formation [6]. Examples of specimens before heat treatment and after successful infiltration are shown in Fig. 1. When infiltration was unsuccessful, the molten metal separated from the powder to form a separate puddle in the bottom of the boat. Partial infiltration, as indicated in Fig. 2, was characterised by an un-infiltrated region in the centre of the specimen.

Oxides and covalent-bonded ceramics could not be infiltrated by molten Cu. A number of transition metal compounds, notably NbC, Cr_3C_2, WC, NbB_2 and Cr_2N, were, however, successfully infiltrated. When the experiments were repeated in air, infiltration was impossible in all cases. The agreement between contact angle data and infiltration behaviour is good but not complete, for example SiC and ZrB_2 did not infiltrate and NbB_2 did partially infiltrate.

Examples of infiltrated ceramics are shown in Figs 3 and 4 for Cr_3C_2 and WC powders respectively. The micrographs show that Cu has penetrated through the interstices to produce samples free from gross macroscopic porosity. Fig. 3, however, shows that there are a few micropores at the particle-matrix interfaces. In all the successfully infiltrated samples, the particle-matrix interfaces appeared to be free from reaction products and energy dispersive x-ray (EDX) analysis showed that the metal matrices were free from Fe, Ni, Nb, W and Cr.

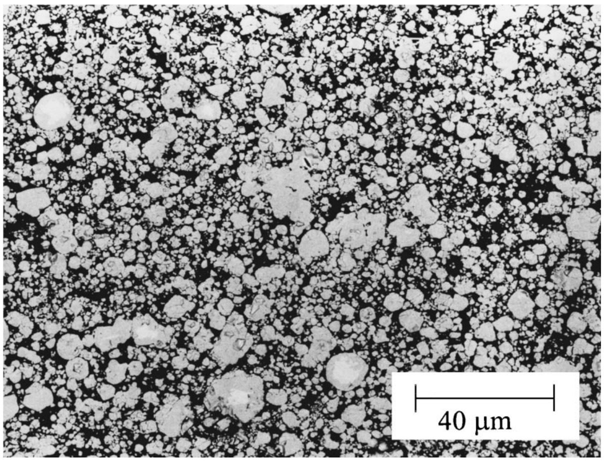

Figure 4 Back-scattered electron image of WC (light) spontaneously infiltrated by Cu (dark).

4. Discussion

Since there was no gas pressure build-up in the furnace, and thus the pressures inside and outside the Cu tube were equal, only the pressure exerted by the metallostatic head of molten Cu above the powder could assist infiltration. This pressure is extremely small, less than 0.2 kPa, compared to pressures of the order of 500–600 kPa [1, 7] that have been identified as being necessary to infiltrate non-wetting Al-ceramic systems. It is, therefore, assumed that any flow of metal into the powder interstices must have been as a result of favourable wetting conditions.

As soon as the Cu melts, if there is no wetting between the metal and the ceramic powder, the molten Cu drains away from the ceramic due to the geometry and positioning of the specimens. Any infiltration must, therefore, be due to instantaneous wetting of the ceramic by the liquid, since liquid-state, wetting-enhancing reactions are unable to take place given the extremely short contact time. EDX analysis of the infiltrated samples showed that there was no contamination from the boat and no reaction or dissolution of the ceramic phases in either the solid state during pre-heating, or when molten.

It was impossible to infiltrate oxides and covalent-bonded compounds. Contact angle data suggest that molten Cu should not readily wet these compounds, with the exception of SiC, at these temperatures. Ionic and covalent solids are characterised by a closed, stable electronic configuration of atoms and high strength inter-atomic bonds. Interactions with these bodies and molten metals is thought to be possible only through partial or complete dissociation of the inter-atomic bonding and chemical reaction with the solid phase [5]. Since copper does not form stable binary carbides or borides and not a particularly stable nitride, $\Delta H_{\mathrm{f,298\,K}} = -75$ kJ mol^{-1} [6], we would not expect it to participate in wetting-enhancing reactions. The solubility of carbon in molten Cu is extremely low and this also reduces its tendency to wet covalent-bonded carbides.

An acute contact angle for Cu on SiC is reported [5] as a result of reaction between molten copper and SiC to produce a Cu-Si intermetallic. For the reasons given earlier, liquid-phase reactions are unable to take place if wetting is not instantaneous, and thus reactive infiltration of SiC can not proceed.

Spontaneous infiltration of a number of transition metal compounds was possible. Transition metal carbides, borides and nitrides tend to have more uniform distributions of electron densities and hence bonding which is more metallic in character [5]. Compounds with metal-like bonding can achieve inter-phase bonding without the need for dissociating bonds within the solid phase. The wettability of these ceramics is good and we would expect them to be spontaneously infiltrated by molten metals. Copper, whilst having the advantage of not forming a tenacious oxide film, has a stable, closed 3d electron orbital resulting in a reduced propensity to form metallic bonds, with elements or compounds, compared to other transition metals.

Contact angle data for Cu droplets on transition metal compounds, as presented in Table I, indicate that several transition metal compounds, NbC, Cr_3C_2, WC, ZrB_2 and Cr_2N, mostly those with less negative heats of formation, have acute contact angles. The heat of formation gives an indication of the energy required to break bonds. Compounds that dissociate bonds more readily are expected to interact more strongly and have smaller contact angles. This trend has been observed for the wetting of ceramics by molten aluminium [4] and several other metals [5].

Whilst room temperature heat of formation data are not accurate indicators of infiltration behaviour, there is reasonably good, although not complete, correlation between contact angle data obtained from simple sessile droplet tests and infiltration behaviour. This is not the case for reactive metals such as Al. Good agreement in the case of copper metal systems is likely to be due to the relative ease with which oxide films can be prevented from forming on molten copper during both sessile droplet experiments and infiltration processing.

There are a number of possible explanations for the discrepancies between infiltration behaviour and contact angle data. Contact angle values presented in the literature are normally equilibrium values, measured after long holding periods under high vacuum. To more accurately predict the infiltration behaviour observed during this work, instantaneous values measured in an argon atmosphere are more appropriate.

Deviations from stoichiometry and contamination may also have resulted in changes in the infiltration behaviour. A shift in the stoichiometric ratio towards excess metallic element [5, 8] enhances the metallic character of the bonding and subsequently improves the wetting between the ceramic and the liquid metal. Powder contamination, in the form of moisture adsorption, may lead to oxidation of the powders during processing. Experiments conducted without argon shielding demonstrate that transition metal compounds readily react in air to produce non-wettable oxides [4].

5. Conclusions

Infiltration trials have been conducted by filling Cu tubes with ceramic powders and melting them under argon. No external forces were applied; successful infiltration of the ceramic relied solely upon favourable metal-ceramic wetting conditions.

Oxides and covalent-bonded compounds were not spontaneously infiltrated but transition metal compounds such as NbC, Cr_3C_2, WC, NbB_2 and Cr_2N were. It was impossible to infiltrate any of these ceramics in air.

Whilst room temperature heat of formation data are not accurate indicators of infiltration behaviour, there is reasonably good, although not complete, correlation between contact angle data obtained from simple sessile droplet tests and infiltration behaviour.

The good correlation is thought to be due to the ease with which the oxide film can be prevented from forming on molten Cu during both sessile droplet experiments and infiltration processing.

Due to the geometry of the process, infiltration requires instantaneous wetting to occur and can not rely on wetting-enhancing reactions. For this reason there will be discrepancies between infiltration behaviour and equilibrium contact angles in reactive systems.

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