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# Interface interaction in the ($B_4C$ + $TiB_2$)/Cu system

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**Abstract** Interface phenomena in the $TiB_2$/(Cu–B) and ($B_4C$ + $TiB_2$)/(Cu–B) systems were investigated in order to determine conditions for cermet preparation by free infiltration. The wetting behavior of the two-phase ceramic substrate may be accounted for as a superposition of behavior patterns characteristic of the two ceramic phases. The relatively low wetting angles of the liquid Cu on the titanium diboride substrate is attributed to a minor departure of the ceramic phase composition from stoichiometry. Copper alloyed with above 8 at.% B yields contact angles less than 20° sufficient for fabrication of cermets based on the two-phase ceramic by free infiltration. The enhanced wetting and the absence of a new phase formation were confirmed by SEM and TEM analysis of the infiltrated cermets.

## Introduction

Ceramic composites based on the two-phase $B_4C$–$TiB_2$ system may be used as corrosion- and wear resistant electrode materials, on account of their high melting points, hardness and good chemical stability. The two-phase ceramic may also be the basis of various metal–ceramic composites (cermets). The interactions that take place at the liquid metal–ceramic interface play a major role in welding procedures and in determining optimal conditions for cermet fabrication. Two-phase ceramic–copper composites [1–3] may also be used as materials for nuclear waste containers on account of the high thermal conductivity of copper and the neutron absorption propensity of the ceramic phases. Successful fabrication of the cermets by free infiltration of porous two-phase ceramic preforms, depends on the ability of the metal component to wet both ceramic phases. Previous studies regarding interface interaction between boron carbide substrate and copper alloys [4, 5] have shown that relatively low wetting angles ( < 40°.) may be achieved by alloying copper with boron and silicon and are linked to boron enrichment of a near surface layer of the boron carbide. The presence of relatively low contact angles is insufficient, however, for ensuring successful free infiltration. Complete free infiltration of boron carbide requires boron enrichment of the ceramic matrix and was achieved by generating the two-phase ceramic that consists of boron-rich boron carbide $B_xC$ ($4 \le x \le 10$) and $TiB_2$. The present paper reports the results regarding the interaction of these ceramic phases with Cu–B alloys and the wetting behavior in this system.

## Experimental

Wetting experiments were performed using the sessile drop method at 1423 K for 30 min in a vacuum furnace (~$10^{-3}$ Pa). A $TiB_2$ hot pressed substrate (97.6% purity) (SINTEC Keramik USA®) and hot pressed boron carbide substrate with near-theoretical density obtained from $B_4C$ powder (Stark®, 97% purity) were used. The two-phase ceramic containing boron carbide

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and titanium diboride was sintered in order to obtain preforms with various (70–96%) relative densities [6]. The samples with near theoretical density were used for wetting experiments, while the porous samples were used for cermet fabrication by free infiltration. A Cu–B master alloy (25 at.% B) was prepared using Cu (99.999% purity) and B powder (99.90% purity) in an arc furnace. Other alloys were prepared in-situ by co-melting of copper with an appropriate amount of a master alloy. The substrates for wetting experiments were polished to the 0.25 μm diamond paste level and cleaned ultrasonically. Contact angles were measured directly from the magnified profile digital images of the molten metal drop. The structure and composition of interfaces were studied by a Jeol JSM 5600 SEM (scanning electron microscopy) equipped with a Noran EDS (energy dispersive spectrometry) and WDS (wavelength dispersive spectrometry) analysis by a Jeol JSM 35C micro probe analyzer. The composition of a near ceramic–metal interface area and of the solidified drop surface was determined also by a PHI 549 AES (Auger Electron Spectroscopy) analyzer accompanied with Ar sputtering depth profiling. The microstructure of the infiltrated cermets was characterized by SEM and a Jeol-JEM -2010 TEM (Transmission Electron Microscope) equipped with Noran EDS analyzer.

## Results

The wetting behavior in the $B_4C$/(Cu–B) system has been reported in a previous communication [5]. It was established that the final apparent contact angles are attained after 10 min of contact and depend on the boron content in the alloy (Fig. 1). A recurring feature of $B_4C$–Cu interface is the formation of a crater in the ceramic substrate due to the strong interaction between molten copper and $B_4C$ (Fig. 2a). The crater contained dark precipitates which were identified as carbon agglomerates. In the solidified copper drop the gray inter-granular phase was boron that precipitated during solidification.

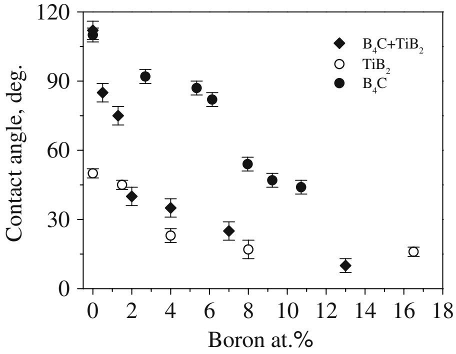

**Fig. 1** The equilibrium contact angle for various substrates as a function of Cu–B alloy compositions (1423 K, 30 min)

For the $TiB_2$/Cu system an equilibrium contact angle of 50°. was observed (Fig. 1) after ~30 min of contact. Boron additions to copper above 8 at.% significantly reduced the contact angle to ~20°. The wetting behavior in the ($B_4C$ + 40% vol. $TiB_2$)/Cu system was similar to that of $B_4C$/Cu and a high apparent contact angle, close to 110°. was observed (Fig. 1). The contact angle drops rapidly with boron additions and its value reaches about 10°. for a boron content of 13 at.%. In the $TiB_2$/Cu system, an undamaged and flat interface with a roughness similar to that of the substrate before its contact with the melt is preserved (Fig. 2b). It is noteworthy that near the free surface of the solidified drop, (the liquid–vapor interface), a thin layer containing titanium and boron, was detected by AES depth profiling. The thickness (10 nm) of this discontinuous layer provides evidence that during the wetting process titanium and boron dissolve in the liquid copper drop and segregate at the liquid–vapor interface (Fig. 3). Apparently titanium forms an oxide at the surface of the molten copper by a reaction with residual oxygen in the experimental chamber. In the $TiB_2$/(Cu–B) system, a minor titanium dissolution was detected adjacent to the ceramic–metal interface (Fig. 4). According to WDS analysis, the dissolution of Ti seems to be only slightly dependent on the boron content in the melt. AES analysis at the free surface of the metal drop in the $TiB_2$/Cu system showed increased surface Ti enrichment as compared to the $TiB_2$/(Cu–B) system (Fig. 5). At the interface between the two-phase ceramic and pure copper, a crater formation was also observed (Fig. 2c). The crater contains copper, $TiB_2$ particles and carbon agglomerates.

In the $B_4C$/(Cu–B) and ($B_4C$ + 40%$TiB_2$)/(Cu–B) systems, boron carbide decomposition and the crater formation were avoided by alloying Cu with 3 and 1.3 at.% B, respectively (Fig. 6a, b).

The interface between the two-phase ceramic and the molten metal of the cermet, fabricated by free infiltration of a porous ceramic preform with a eutectic Cu–13 at.% B alloy, was examined by transition electron microscopy (TEM). The microstructure of the cermet is shown in Fig. 7. The TEM image (Fig. 8) shows that even very thin capillaries between two $TiB_2$ particles are completely filled with the Cu–B alloy, with no new phase formation, providing proof that the infiltration process was fully completed.

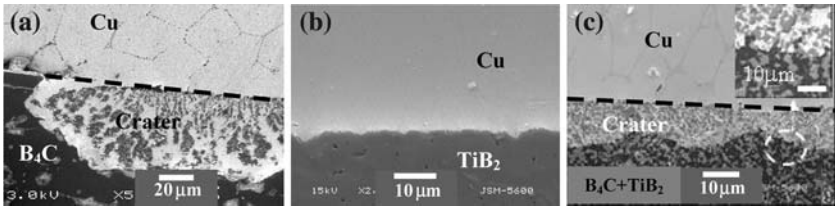

**Fig. 2** SEM images of the ceramic–Cu interfaces after wetting experiments (1423  K, 30 min): (**a**) $B_4C$, (**b**) $TiB_2$, (**c**) $B_4C$ + $TiB_2$. The initial metal–ceramic interfaces in (**a**) and (**c**) are marked by dashed lines

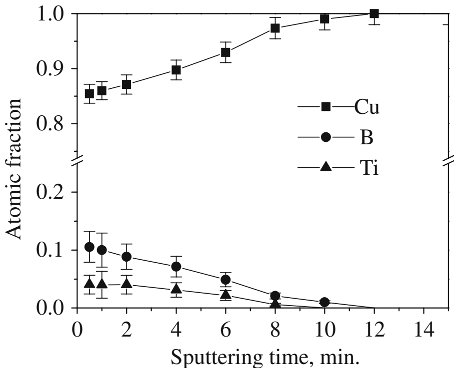

**Fig. 3** AES depth profile from the free surface of the solidified copper drop being in contact with $TiB_2$ at 1423 K, 30 min (sputtering rate ~1 nm/min)

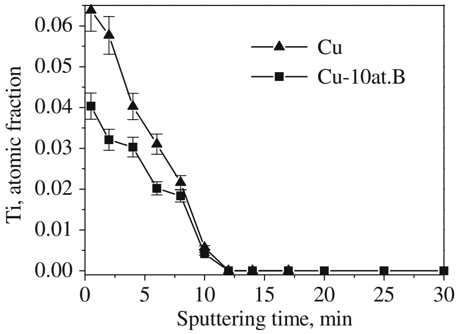

**Fig. 5** Titanium content on the free surface of the solidified drops of pure Cu (1) and Cu-10at%B (2) being in contact with $TiB_2$ at 1423 K, 30 min (AES depth profile, sputtering rate ~1 nm/min

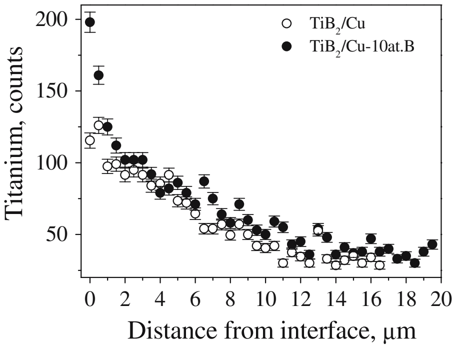

**Fig. 4** Titanium WDS line scan taken from $TiB_2$/Cu (1) and $TiB_2$/(Cu-10at%B) (2) interfaces

## Discussion

The wetting behavior and the interface interaction between the two-phase ceramic and Cu–B melts can be described in terms of the properties of the individual $B_4C$/(Cu–B) and $TiB_2$/(Cu–B) systems.

The details of the thermodynamic analysis of the $B_4C$/(Cu–B) system have been reported by Froumin et al. [5]. The calculated isothermal section of the copper-rich corner of the ternary Cu–C–B diagram at 1423 K showed that $B_4C$ is in equilibrium with graphite and with the Cu–2.4 at.%B liquid solution. Boron rich boron carbide ($B_{10}C$) is in equilibrium with boron saturated by copper and with the Cu–12.9 at.%B liquid solution. According to the analysis, copper alloyed by boron (B > 2.4 at. %) prevents the decomposition of the $B_4C$ substrate and a flat interface is maintained. Concomitantly, the near surface boron carbide composition is altered towards higher boron content that depends on the boron content of the melt (Fig. 9).

Titanium diboride exists over a narrow but finite composition range ($TiB_{1.9}$–$TiB_2$). In a previous study [7], it was shown that in equilibrium with stoichiometric titanium diboride, the titanium concentration in the copper melt is extremely low ($1 \times 10^{-7}$ at. %). This value is related to the very low activity of Ti in the $TiB_2$ phase. According to Misra [8], at 1273  K for the boron rich edge of the $TiB_2$ phase, the Ti activity value ($a_{Ti}$) is equal to $5.22 \times 10^{-13}$. At this composition, the activity of B ($a_B$) in equilibrium with pure B equals one. At the Ti-rich composition of the titanium diboride phase ($TiB_{1.9}$), the activity of Ti is much higher ($1.74 \times 10^{-4}$), while the activity of B decreases to $5.48 \times 10^{-5}$. Thus, the equilibrium titanium content in the melt that is in contact with the titanium rich boride increases significantly to reach 0.07 at.%. Such minor departure of titanium diboride from the stoichiometric composition is sufficient to generate a contact angle close to 50°. (Fig. 1). Similar effects linked to the departure of the ceramic phase from

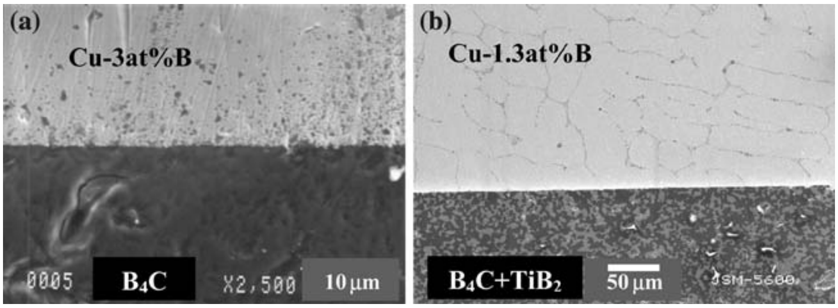

**Fig. 6** SEM images of the ceramic–(Cu–B) drop interfaces after wetting experiments (1423 K, 30 min): (**a**) $B_4C$ and (**b**) ($B_4C$-$TiB_2$

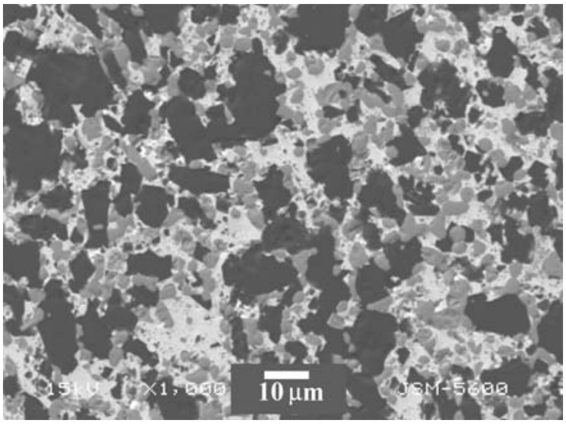

**Fig. 7** Backscattered electrons SEM image of the infiltrated cermet. Dark particles – $B_4C$, gray particles – $TiB_2$, bright phase – (Cu–B) infiltrating alloy

stoichiometric composition have been reported in numerous studies (e.g. TiC/(Cu, Sn and Cu,Sn–Ti) [9], TiC or TiN(Cu, Ag and Cu, Ag–Ti) [10]).

According to the binary Cu–B phase diagram, copper dissolves about 22 at.%B at 1423 K. Thus, the dissolution of boron in liquid copper has to be taken into account. Calculation of the chemical potential of boron [5] in the melt allowed concluding that in equilibrium with $TiB_{1.9}$, liquid copper contains only 0.001 at.%B, whereas in equilibrium with $TiB_2$ the boron content raises to 8.7 at.%B. According to our experimental results the melt contains detectable amounts of titanium and traces of boron. This composition is far from equilibrium of the melt with the stoichiometric diboride. In summary, it ensues from the composition of the metal drop that had been in contact with the boride substrate used in the present study (Fig. 3), that the composition of the boride is closer to $TiB_{1.9}$ than to $TiB_2$.

The wetting behavior of the two-phase ceramic substrate by low boron content Cu–B alloys (less than ~1.3 at.%B) is altered by dissolution of the boron carbide and graphite precipitation at the interface (Fig. 2c). At higher boron contents, at which no dissolution of $B_4C$ occurs, wetting is governed by the properties of the $TiB_2$/(Cu–B) system. The excellent wetting and the absence of a new phase formation in this system were confirmed by SEM and TEM analysis of the infiltrated cermets.

## Conclusions

The interface phenomena in the $TiB_2$/(Cu–B) and ($B_4C$ + $TiB_2$)/(Cu–B) systems were investigated in order to define the conditions of the cermets preparation by the free infiltration approach. The relatively low

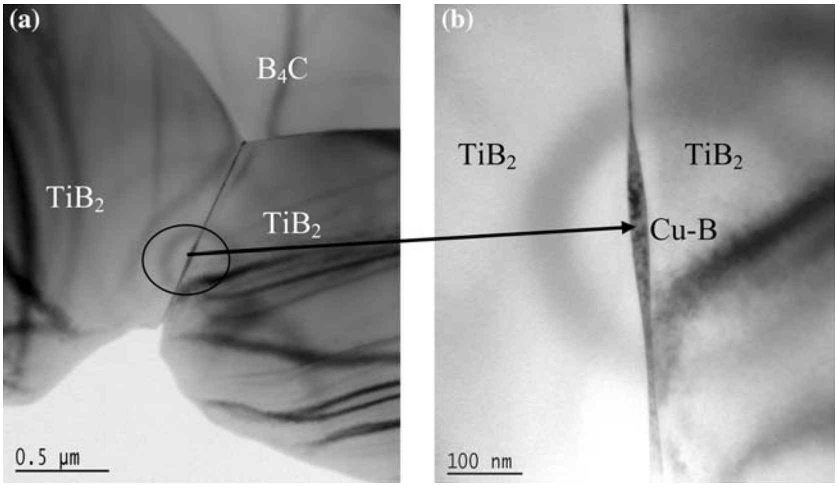

**Fig. 8** TEM micrograph of the infiltrated cermet. Thin capillary between two adjacent $TiB_2$ particles (**a**) is completely filled with metal (**b**)

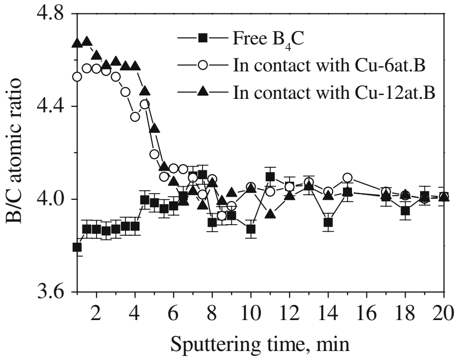

**Fig. 9** B–C ratio at substrate near interface layers after contact with Cu–B melt (derived from AES depth profiles): 1-$B_4C$ free surface before interaction, 2-Cu-6 at.%B and 3-Cu-12 at.%B (sputtering rate 20 nm/min). Standard error bars characteristic for the Auger measurements are given in the case of the free $B_4C$ surface

wetting angles of liquid copper-alloys on the titanium diboride substrate are attributed to a minor departure of the ceramic phase composition from stoichiometry. The wetting behavior of the two-phase ceramic substrate may be accounted for in terms of a superposition of the behavior patterns characteristic of the two individual ceramics. At low boron content (less than 1.3 at.%) in the melt, the behavior of the two-phase ceramic substrate is similar to that of the $B_4C$/(Cu–B) system, in which wetting is controlled by the decomposition of the $B_4C$ and the formation of a crater at the ceramic–metal interface. Above this boron content, the initial flat interface is preserved and the wetting behavior resembles that of the $TiB_2$/(Cu–B) system. The excellent wetting and the absence of a new phase formation were confirmed by SEM and TEM analysis of the infiltrated cermets.

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