PROCEEDINGS OF THE IV INTERNATIONAL CONFERENCE/HIGH TEMPERATURE CAPILLARITY

JOURNAL OF MATERIALS SCIENCE **40** (2005) 2325–2327

Interface phenomena in the B_4C/(Me-Ti) systems (Me = Cu, Au and Sn)

M. AIZENSHTEIN, N. FROUMIN, N. FRAGE, M. P. DARIEL
Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel

Interface structure and wetting behavior in the B_4C/(Me-Ti) (M = Cu, Sn, Au) systems depend on boron solubility in the melt and new phase formation at the interface. Wetting in the B_4C/(Cu-Ti) system may be attributed to direct contact between TiB_2, formed at the interface, and the melt. The equilibrium wetting angle in the B_4C/(Sn-Ti) and B_4C/(Au-Ti), reflects probably the formation of a TiC_x layer with a carbon content determined by the activity of titanium in the melt. *© 2005 Springer Science + Business Media, Inc.*

1. Introduction

It is well known [1, 2] that the wetting of non-oxide ceramics by non-reactive metals can be improved by an addition of a reactive component that may alter the metal-ceramic interface. In a previous communication [3], the effect on the interface phenomena of Si additions to liquid Cu in B_4C/Cu-Si system was discussed. It was established that Si dissolved in the melt, reacts with carbon that originated from the boron carbide, resulting in the formation of SiC and in altering the boron carbide composition towards higher boron content. This feature, together with the formation of a crater at the metal-ceramic interface due to the significant boron solubility in liquid Cu, governs the wetting behavior in this system. The addition of Ti to non-reactive metals may also change the boron carbide/melt interface. On account of the high affinity of titanium for boron, the formation of the TiB_2 phase and of graphite takes place at the interface rather than that of TiC. The effect of titanium additions to the liquid non-reactive metals (Cu, Au, and Sn) on the interaction between boron carbide and the melts and the wetting behavior in these systems are described and discussed in the present study.

2. Experimental procedures

The B_4C ceramic sample preparation and details of the wetting experiments are reported elsewhere [4]. Me-Ti alloys (99.999% pure) with the Ti concentration range up to 8 at% were prepared *in situ*. The solidified drops were cross-sectioned and the structure of the metal-ceramic interface was studied using SEM equipped with EDS/WDS analyzers.

3. Experimental results and discussion

The steady-state contact angles as a function of the titanium content in the melts are shown in Fig. 1. Small amounts of Ti additions to Cu and Sn (<1 at%) lead to good wetting ($\Theta < 30$ degree). This same value of the contact angle for the Au-Ti melt is reached, however, at a titanium concentration higher than 4 at%.

At the B_4C/(Sn-Ti) interface a new and discontinuous reaction product was detected (Fig. 2a). This new phase, as determined at a higher magnification, consists of two layers. Qualitative WDS scan (Fig. 2b) shows that the double layer, which is attached to the substrate, namely at approximately 12 to 17 μm from the beginning of the scan contains Ti and B, while the large Ti and C peaks, at the starting point of the scan, are due to the presence of isolated TiC particles floating within the melt. The cross section of the B_4C/(Au-Ti) interface is shown in Fig. 3a. In this system, according to WDS line scans (Fig. 3b) the product of the interaction between the melt and the boron carbide substrate also consists of two very thin and strongly adhering $TiB_2$and TiC layers.

The interface between B_4C and Cu-Ti melt (Fig. 4) is quite different from the interfaces presented in the Figs 2 and 3. The interaction at the interface leads to significant substrate dissolution in the melt and to crater formation. The crater is filled with graphite agglomerates distributed in the melt. At a certain distance from the initial metal/ceramic interface, the presence of a convoluted "lace" approximately 30 μm wide and consisting of TiB_2 particles was observed. The titanium content in the solidified metal below the "lace", as well as in the crater, was lower than in the volume of the metal drop. The "lace" is separated from the initial interface along the whole width of the drop except in the very vicinity of the triple line where it appears to be anchored to the B_4C substrate (Fig. 4b).

The experimental results, which were obtained for various non-reactive metals, may be well accounted of by a thermodynamic analysis of the binary Me-B and Me-Ti liquid alloys and their interaction with the solid boron carbide substrate. The starting point of the discussion is the greatly varying solubility of B in the molten metals. Pure Cu dissolves about 25 at% B at 1200°C, the boron solubility at the same temperature in liquid Au is less than 1% at.% and in liquid Sn it is only few ppms [5, 6]. The decomposition of boron carbide in contact with Cu-Ti and the interface morphology

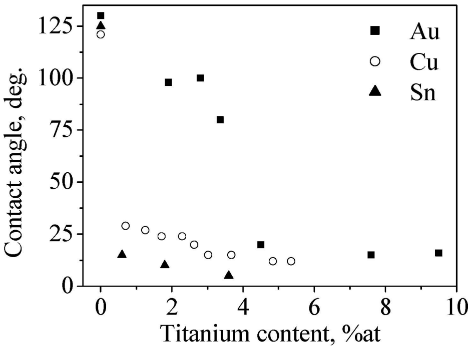

Figure 1 The equilibrium contact angle at 1423 K as a function of titanium content in the melts.

(Fig. 4) is controlled by the high boron solubility in the melt. In the case of Sn and Au the interface structure and composition are determined by a direct interaction between Ti dissolved in the melt and the B_4C substrate (Figs 2 and 3). Since the affinity of Ti to B and C, respectively, is so much stronger than to Cu, in a first approximation, the experimental results may be explained by the analysis of a schematic ternary B-C-Ti phase diagram (Fig. 5) [7]. The sequence of phase formation when pure Ti reacts with the stoichiometric boron carbide phase may be understood by following the dashed line, which links the Ti corner of the diagram with the point corresponding to boron carbide. Each point on this line defines relative amounts of the reacting phases. At a low Ti /B_4C mass ratio, the system is located in the three phase region (I) $TiB_2 +$ graphite $+ B_4C$. Thus, first phases that are formed at the boron carbide/Ti interface are TiB_2 and graphite. The formation of the TiC phase takes place only when boron carbide (locally) has reacted completely and TiC is in equilibrium with TiB_2 and graphite (region II). At higher Ti content the conditions for coexisting TiB_2 with non-stoichiometric

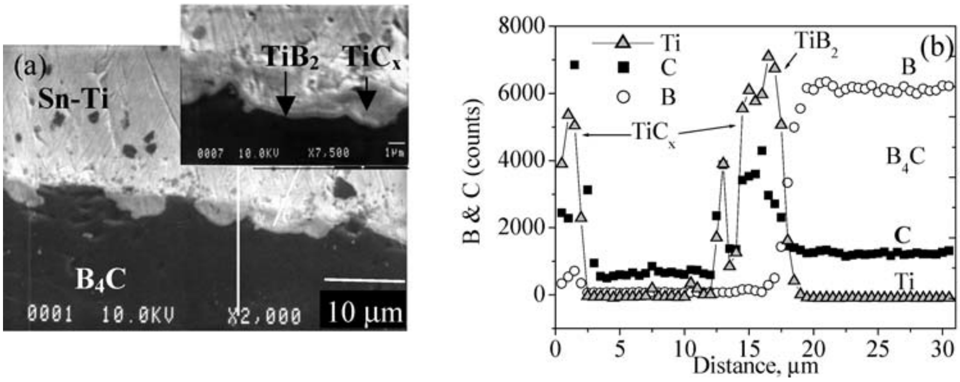

Figure 2 SEM micrographs (a) and WDS line scan (b) of the B_4C/(Sn-Ti) interface.

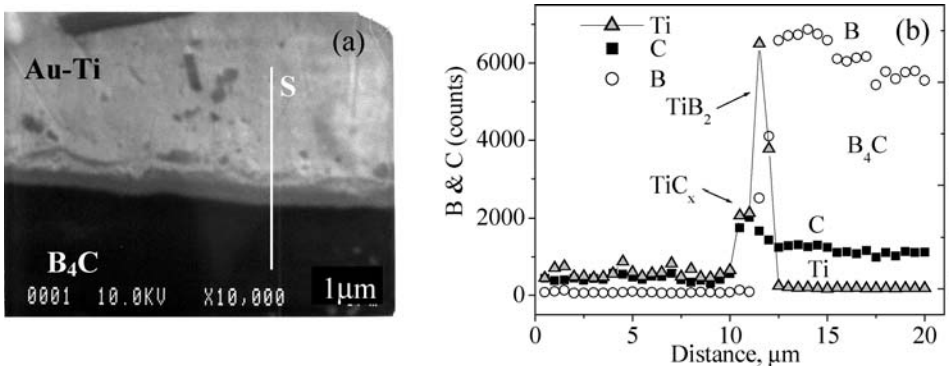

Figure 3 SEM micrograph (a) and WDS line scan (b) of the B_4C/(Au-Ti) interface.

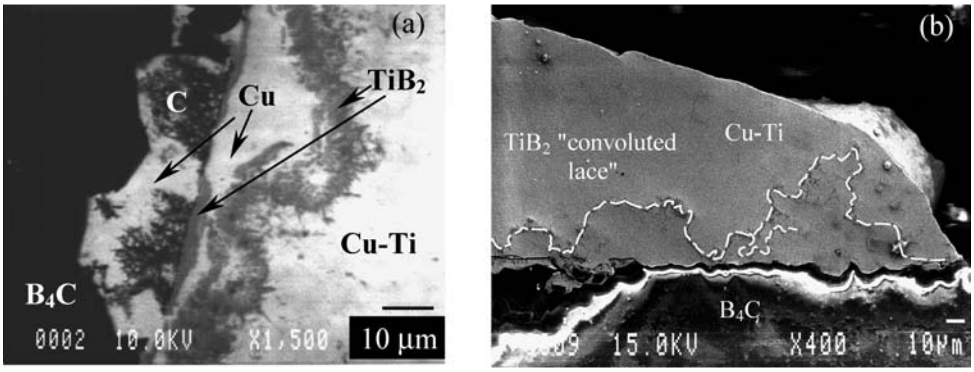

Figure 4 SEM micrographs (a) the interface morphology: $B_4C +$ graphite $+ TiB_2 +$ Cu (Ti) solution are observed (b) The position of the TiB_2 layer in respect to the drop and to the substrate.

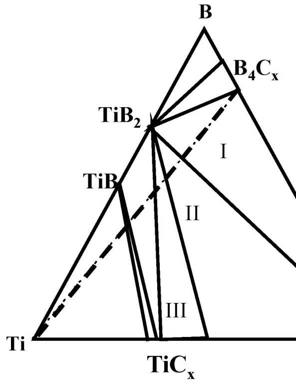

Figure 5 Schematic view of the B-C-Ti ternary phase diagram at 1400 K I—TiB_2 + graphite + B_4C, II—TiB_2 + graphite + TiC, III—TiB_2 + TiC_x.

titanium carbide TiC_x phase may be achieved. According to this analysis the formation of TiC-TiB_2 bi-layered structure (Fig. 3b) at the boron carbide substrate may take place if there is no direct contact between Ti or the titanium containing melt and boron carbide. Such situation arises when Sn-Ti and Au-Ti melts interact with the boron carbide substrate. In these systems, a TiC_x phase is formed in contact with the substrate and the melt actually wets this carbide phase. The composition of the TiC_x layer is determined by the activity of titanium in the melt. The wetting of TiC_x is affected significantly by its carbon content (the contact angle decreases with a decreasing x value [8]) and the latter is determined by the activity of titanium in the melt [9]. The activity of titanium in the Au-Ti melt is significantly lower than in the Sn-Ti molten solution [10, 11]. That is the reason for having, at the same titanium content in the melt, a lower x value of TiC_x in equilibrium with the Sn-Ti solution than in equilibrium with the Au-Ti melt. This also accounts for the higher titanium content in the Au-Ti melt necessary for reaching the same equilibrium contact angle as in the Sn-Ti solution [8].Several aspects in these systems remain unexplained. The role of the triple line in the B_4C/Sn-Ti and B_4C/Au-Ti systems is not yet well defined. Thus it is possible that the melt at the triple line is in contact with a TiB_2 layer and not only with TiC_x layer. In contrast, the continuous dissolution of the B_4C in the Cu-Ti melt, due to the high boron solubility, leads to direct contact with B_4C and no TiC phase is formed. In this case the equilibrium contact angle is established by direct contact between TiB_2 and the liquid at the triple point. The peculiar morphology of the convoluted TiB_2 lace requires further study; in particular, its formation and its growth have to be accounted for.

4. Conclusions

Interface structure and wetting behavior in the B_4C/(Me-Ti) systems depend on boron solubility in the melts and new phase formation at the interface. Wetting in the B_4C/(Cu-Ti) system may be attributed to direct contact between TiB_2 and the Cu-Ti liquid solution at the triple line. The equilibrium wetting angle in the B_4C/(Sn-Ti) and B_4C/(Au-Ti) reflects, probably, the formation of TiC_x layer with a carbon content depending on the titanium activity in the melt.

Acknowledgment

This research was partially supported by the Israeli Ministry of Science by grant No. 20562-01.

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Received 31 March
and accepted 18 July 2004