Rim region growth and its composition in reaction bonded boron carbide composites with core-rim structure.

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Abstract. Aluminum was detected in reaction-bonded boron carbide that had been prepared by pressureless infiltration of boron carbide preforms with molten silicon in a graphite furnace under vacuum. The presence of Al₂O₃ in the heated zone, even though not in contact with the boron carbide preform, stands behind the presence of aluminium in the rim region that interconnects the initial boron carbide particles. The composition of the rim corresponds to the Bₓ(C,Si,Al) quaternary carbide phase. The reaction of alumina with graphite and the formation of a gaseous aluminum suboxide (Al₂O) accounts for the transfer of aluminum in the melt and, subsequently in the rim regions. The presence of Al increases the solubility of boron in liquid silicon, but with increasing aluminum content the activity of boron decreases. These features dominate the structural evolution of the rim-core in the presence of aluminum in the melt.

1. Introduction

Light ceramics are particularly attractive for personal, land and airborne vehicle armor. High values of hardness are by common consensus of crucial importance for good ballistic resistance. Thus, boron carbide, which has very high hardness and low mass per volume ratio [1], has long been considered as a choice armor material candidate. However, difficulties and costs of fabrication, mainly by hot pressing, are factors of paramount importance in determining whether a particular material is considered for armor applications and limit the extended use of boron carbide based armor.

An alternative way for the fabrication of a fully dense boron carbide composite is the so-called "reaction bonding" process [2,3]. According to this method, a green body of boron carbide with or without free carbon is infiltrated with molten silicon. The reaction of molten silicon with the boron carbide particles or with free carbon leads to the formation of silicon carbide. The final composite consists mostly of the initial boron carbide grains, a newly formed Bₓ₂(B,C,Si)₃ phase, which surrounds the initial boron carbide particles, the SiC phase and some unreacted residual silicon. A typical microstructure of the infiltrated boron carbide composites is shown in Fig 1. Electrochemical etching allowed to reveal the presence of the initial boron carbide particles (core regions) surrounded by the newly formed carbide phase (rim regions) (Fig. 1 insert). The formation of this morphology was attributed to the dissolution-precipitation reactions in the boron carbide - silicon system and has been discussed previously [4].
Fig. 1. SEM micrograph of a typical microstructure of the infiltrated boron carbide composites. SEM micrograph of a electrochemically etched composite (insert) reveals the presence of the initial boron carbide particles (core regions) surrounded by the newly formed carbide phase (rim regions).

The composite material was prepared by pressureless infiltration of boron carbide preforms with molten silicon in a graphite furnace under vacuum. Some alumina parts were present in the heated zone, but none in any contact with the boron carbide preform. Neither the starting boron carbide powder nor the high purity silicon used for infiltration contained any aluminum. Nevertheless, substantial amounts of aluminum were detected by WDS analysis in the rim regions of the composite (Fig. 2).

Fig. 2. Line-scan along the straight white line in the backscatter electron image of boron carbide composite.
The presence of aluminum affects to a considerable extent the morphology and the content of the rim region in the composite. The present work was undertaken in order to gain insight in the mechanism whereby aluminum is transported and makes its appearance in the rim region and in order to study its effect on the rim growth kinetics.

2. Experimental procedure

Two sets of ceramic preforms (20 mm diameter and 3 mm height) were made (compacting under uniaxial pressure of 25MPa.) from coarse boron carbide powder (average size of about 106μm, "Mudan Jiang" Chinese company) and infiltrated with molten silicon (Alfa Aesar 99.9999%).

The infiltration was conducted in a vacuum furnace (10⁻⁵ torr) at 1753K and the holding at the infiltrating temperatures varied from 10 to 240 min. The infiltration was carried out by placing an appropriate silicon lump on the top of the porous preforms. In the first set of the experiments, the preforms were placed on a SiC substrate (type-A), in the second set (type-B) Al₂O₃ granules had been placed beneath the SiC substrate. No direct contact whatsoever took place between the alumina granules and the boron carbide preform (Fig. 3).

The microstructure of the samples was studied by optical microscopy (OM, Zeiss Axiovert 25), scanning electron microscopy (SEM, JEOL-35) in conjunction with an energy-dispersive spectrometer (EDS) and a wavelength-dispersive spectrometer (WDS). The phase composition and the structure of the samples was analyzed by X-Ray diffraction (XRD), using a Rigaku RINT 2100 diffractometer with Cu Kα radiation. The scanning angle 2θ was increased in a step of 0.02°.

3. Result and discussion

3.1. Phase composition

The XRD patterns of the type-A and type-B composites, as a function of holding time at the infiltrating temperature, are presented in Fig. 4. According to the XRD results, the type-A specimens that have been infiltrated in Al₂O₃-free conditions, consist of four phases namely, boron carbide (B₄C), a ternary B-C-Si carbide phase, β-SiC and residual silicon. It is noteworthy that the position and the shape of the peaks corresponding to the ternary carbide do not change with the holding time. These peaks correspond to the B₁₂(B,C,Si)₃ phase [5,6,7].

For type-B specimens that had been infiltrated in the presence of Al₂O₃, the evolution of the phase composition is different. First, an additional relatively broad peak (2θ=38.5) appeared after a 30 min heat treatment. This peak may be attributed to an aluminum based solid solution. The intensity of the peaks corresponding to the boron carbide phase decreases, while the peaks attributed to the new formed carbide phase Bₓ(C,Si,Al)ᵧ increase with time. These changes suggest that substantial transformation of the initial boron carbide particles to the newly formed carbide phase took place. After a four hour-long heat treatment, the boron carbide peaks disappear, indicating an almost
complete transformation into a new structure. In contrast to type-A composites, in which the position and the shape of the peaks corresponding to the ternary carbide do not change, in type-B samples, the peaks corresponding to the new formed carbide phase shift towards lower angles. Furthermore, the shape of these peaks indicates that the rim region consists of several layers with varying lattice parameters, layers that were formed during the holding time (Fig. 4.).

3.2. Origin of aluminium in the melt.
The presence of aluminum in the composite having been unequivocally demonstrated, it was necessary to account for its transport from the alumina particles into the composite. The starting point of the model is based on the chemical interaction between alumina and graphite that is expressed by the following equations:

\[
\begin{align*}
A_l O_{(s)} + C_{(s)} &= A_l O_{(g)} + CO_{(g)} \\
A_l O_{(g)} &= 2[A_l] + 0.5O_2{_{(g)}} \\
C_{(g)} + CO_{(g)} &= 2CO_{(g)} \\
CO_{(g)} + 0.5O_2{_{(g)}} &= CO_2{_{(g)}}
\end{align*}
\]

where \(s\) and \(g\) denote solid and gaseous phases, respectively, and the square brackets denote that the element is in a liquid solution.

In the quaternary Si-Al-O-C system with four phases, namely the liquid solution, alumina, graphite and the gaseous phase are in equilibrium, the degree of freedom at constant temperature (\(F = 4+1-4\)) is equal to 1. The partial pressure of \(A_l_2O\) is therefore a function of the aluminum content in the liquid solution. This function may be derived from the equilibrium constants of the reactions (1-4)

\[
K_1 = P_{CO_2}P_{Al_2O}, \quad K_2 = \frac{P_{O_2}^{0.5}A_{Al}^{2}}{P_{Al_2O}}, \quad K_3 = \frac{P_{CO}^2}{P_{CO_2}}, \quad K_4 = \frac{P_{CO_2}}{P_{CO^2}P_{O_2}^{0.5}}
\]
\[ \ln P_{\text{Al}_2\text{O}} = 4 \ln a_{\text{Al}} + \ln \left( \frac{K_3}{K_1} \left( \frac{K_2}{K_1} \right)^2 \right) \]  

where \( a_{\text{Al}} \) stands for the activity of aluminum in the melt. The equilibrium constants were calculated according to thermodynamic data, presented in Table 1.

The calculated values of \( P_{\text{Al}_2\text{O}} \) as a function of aluminum activity in the melt at 1753K are presented in Fig. 5. The horizontal line corresponds to the vacuum level in the furnace, which is about \( 1.3 \cdot 10^{-8} \text{ atm} \).

| Reaction | \( \Delta G^0(1) \) | \( \Delta G^0(2) \) | \( \Delta G^0(3) \) | \( \Delta G^0(4) \) |
|----------|------------------|------------------|------------------|------------------|
| \( \Delta G^0 \), kJ/mole | 1066.03-377.727T | 226.73 + 0.049T | 169.0172T | -282.69 + 0.086T |

Since the equilibrium partial pressure of \( P_{\text{Al}_2\text{O}} \) is higher than the total pressure in the furnace, reaction 1 takes place, alumina decomposes and aluminum is being transferred via the gaseous phase into the melt. It has to be noted that this process may occur without direct contact between graphite and alumina. Thus, according to the results of the thermodynamic analysis, the interaction between graphite and alumina stands at the origin of the presence of aluminum in the melt.

3.3. Rim growth kinetics.

The microstructural evolution of the type-A and type-B composites in the course of the heat treatment for various durations may be followed using the SEM micrographs shown in Fig 6. All the samples were electro-chemically etched in KOH solution in order to emphasize the difference between rim and core regions.
| Holding Time, min | Type-A | Type-B |
|-------------------|--------|--------|
| 10                | ![SEM micrograph of type-A composite](image1) | ![SEM micrograph of type-B composite](image2) |
| 30                | ![SEM micrograph of type-A composite](image3) | ![SEM micrograph of type-B composite](image4) |
| 60                | ![SEM micrograph of type-A composite](image5) | ![SEM micrograph of type-B composite](image6) |
| 240               | ![SEM micrograph of type-A composite](image7) | ![SEM micrograph of type-B composite](image8) |

Fig. 6. SEM micrographs of *type-A* and *type-B* composites that electro-chemically etched in KOH solution in order emphasize the differences between rim and core regions.
For *type-A* composites, the thickness of the rim layer shows a very weak dependence on the holding time, while for *type-B* composites substantial widening of this region takes place. In *type-B* specimens, after 60 min most initial boron carbide particles are transformed into the quaternary carbide phase \( B_x(C,\text{Si},\text{Al})_y \) [9]. These microstructural observations are in a good agreement with the results of the XRD analysis. According to the microstructural observations, it appears that in *type-A* composites the dissolution precipitation process operates only during the initial stages of the heat treatment. The rim region has a coherent boundary with the initial boron carbide particles [4] and prevents the continuous dissolution of boron carbide. After about 10 min the transformation of boron carbide to \( B_{12}(B,\text{C},\text{Si})_3 \) and the rim regions growth are, probably, controlled by a diffusion process through the newly formed layer.

The presence of Al significantly changes the rate of growth of the rim region. We suggest that a reason of this feature is the effect of Al on the boron solubility in liquid Si. According to thermodynamic data [8] Al increases the solubility of boron in liquid Si and decreases its activity. Thus, when Al is absorbed in the melt, enhanced dissolution of boron carbide and \( B_{12}(B,\text{C},\text{Si})_3 \), which is formed during the initial stage of infiltration (where aluminum is absent in the melt) takes place. With increasing Al content, the thermodynamic equilibrium requirements dictate additional boron carbide phase dissolution in parallel with the precipitation of the Al and Si containing carbide phase. As a result of this process the rim region consists of a sequence of quaternary carbide layers with various Al contents, as was detected by XRD analysis.

An interesting additional feature was revealed during the electro-chemical etching procedure. In *type-A* samples, the rim regions are always attacked preferably, while for *type-B* samples, after 30 min of holding, the core regions were more likely than the rim regions to be attacked. This feature is attributed to the increased aluminum content within the rim regions that promotes the stability of the quaternary carbide phase in the KOH solution.

**4. Conclusion**

The presence of alumina parts within a furnace with graphite heating elements leads to the presence of aluminum in the composites fabricated by infiltration of porous boron carbide preforms with liquid Si at 1753K under vacuum. The presence of aluminum in the boron carbide–silicon system significantly enhances the transformation of the initial boron carbide particles into a newly formed quaternary carbide phase and the kinetics of the rim-region growth.

**5. References**

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