

Interaction of titanium diboride/boron nitride evaporation boats with aluminium

Mathias Herrmann^{a,*}, Jan Räthel^a, Sören Höhn^a,
Jens Eichler^b, Alexander Michaelis^a

^a *Fraunhofer Institute of Ceramic Technologies and Systems, Dresden, Germany*

^b *ESK Ceramics GmbH & Co. KG, Max-Schaidhauf-Str. 25, Kempten, Germany*

Received 22 December 2010; received in revised form 14 April 2011; accepted 30 April 2011

Available online 23 June 2011

Abstract

Hexagonal boron nitride/titanium diboride composites are widely used as evaporation boats for aluminium deposition to produce functional and decorative layers on different target materials. The lifetime of such a material is limited mainly by the interaction of the metal with the ceramic substrate, but the corrosion mechanism has still not yet been thoroughly investigated and understood. In this article the corrosion mechanism for the evaporation boats used was investigated using thermodynamic calculations, FESEM, EDX and XRD phase analysis. The analysis showed that hexagonal boron nitride (hBN), which is thermodynamically less stable than TiB₂, is passivated during the application process through the formation of AlN surface layers, whereas the thermodynamically more stable TiB₂ phase dissolves and Ti-rich components precipitate in cooler regions of the evaporation boats.

© 2011 Elsevier Ltd. All rights reserved.

Keywords: Composites; Borides; Nitrides; Lifetime; Diffusion

1. Introduction

Thin metallic coatings on glasses, plastics and other components are commonly used for generating new functional (electromagnetic shielding, corrosion-resistant layers, permeation barriers) and decorative applications.¹ One of the most widely used methods for producing these coatings is metallic evaporation or physical vapour deposition. For example, the evaporation of aluminium amounts to an estimated annual volume of around 35 million euros.

For aluminium evaporation ceramic boats (Fig. 1a) heated by direct electric current have been used since the beginning of the sixties.² The most commonly used evaporation boats are made up of two (hBN/TiB₂)^{2–4} or three (hBN/TiB₂/AlN)⁵ components.

TiB₂ is responsible for the electrical conductivity and hBN is necessary for providing the thermal shock resistance. Evaporation boats are heated and cooled down at a rate of up to 1000 K/min. Additionally the evaporation boats normally contain calcium borates.² CaO is added to the starting composition to react with the B₂O₃ existing on the surfaces of hBN and TiB₂. This reaction is necessary to improve the stability of the boats by preventing the formation of B(OH)₃ during post-sintering treatment and storage and the evaporation of HBO₂ and water during the application process.²

The materials usually have a resistivity in the range 100–100 000 μΩ cm. This requires the amount of TiB₂ to be near the percolation limit of typically 30–45 vol.% TiB₂. Thus a small change in the TiB₂ amount leads to a large change in the electrical resistivity of the composite material and the amounts and grain sizes of the components must be precisely controlled. The lifetime of the evaporation boat is usually determined by the corrosion caused by the molten aluminium (Fig. 1b).

The corrosion mechanism is still not completely understood today, mostly due to problems with preparation, prevent-

* Corresponding author. Tel.: +49 351 2553 7527; fax: +49 351 2554 122.

E-mail address: Mathias.Herrmann@ikts.fraunhofer.de (M. Herrmann).



Fig. 1. Typical evaporation boat (a) and photo of an evaporation boat after application (b). The remaining metal is clearly visible.

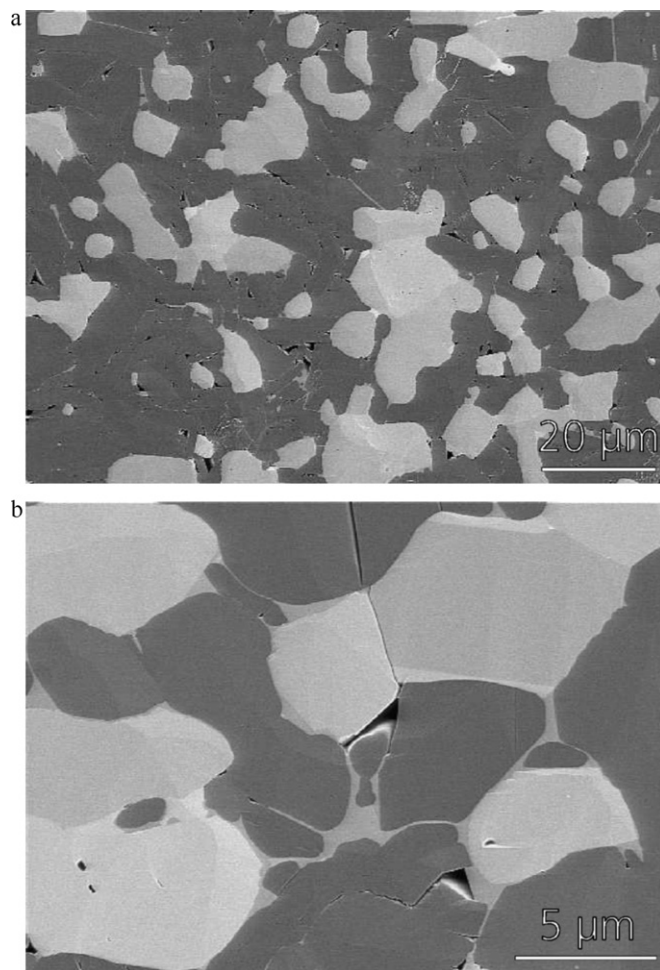


Fig. 2. FESEM micrograph of the hBN/TiB₂ two-component evaporation boat (hBN appears dark gray, TiB₂ appears light gray and the amorphous borate phase appears gray).

ing observation of the undamaged microstructures of the hBN/TiB₂ composites and the metal–ceramic interface. The microstructures of the hBN/TiB₂ composites cannot be prepared using classic polishing techniques.⁶ The method of choice for preparation is ion beam-based polishing⁷ which allows for high-resolution imaging of the hBN/TiB₂ structures. Fig. 2 shows a typical microstructure with TiB₂ (light gray) and hBN (dark gray). An amorphous phase composed of Ca borates (gray) is visible at some of the grain boundaries. Based on the developed method analysis of the evaporation boats used was carried out and the results interpreted using thermodynamic calculations.

2. Experimental

Commercially available evaporation boats (DiMet[®] from ESK Ceramics GmbH & Co. KG) operated in continuous coating equipment for approximately 8 h at 1400–1500 °C were used for ex situ investigation of the interaction between the metallic melt (aluminium) and the hBN/TiB₂ evaporation boat material. After completion of evaporation and cooling down the boat was analysed. To obtain a better view of the types of surface and bulk reactions taking place between metallic melt and substrate material as well as the nucleation sites for newly formed chemical compounds in the cavity of the evaporation boat XRD measurements (XRD 7, CuK α , Seifert FPM, Germany) and SEM investigations (Leo Gemini DSM 982, LEO

Elektronenmikroskopie GmbH, Oberkochen, Germany) were carried out in a first step. In a second step a cross section of a boat was prepared by cutting and pre-polishing followed by removal of the damaged surface using the broad ion beam method (RES 010, Bal-Tec AG, Germany). If classic grinding was used instead of this technique, the strong heterogeneous hardness of hBN/TiB₂ composite members would lead to a heavily damaged microstructure.⁸ Polishing with Ar ions (2 mA at 6 kV) and simultaneously rotating the sample result in a surface showing the true microstructure without any cutting- or grinding-induced damage. The surface of the cavity to be in direct contact with the metallic melt could be analysed without any preparation.

Surface and polished cross sections were investigated using a field emission scanning electron microscope (FESEM) equipped with an EDX detector.

Thermodynamic calculations were also carried out using the FACTSAGE (version 5.1) program⁸ and the SGTE database.⁹ The algorithm calculates the equilibrium phases at a given temperature and pressure by calculating the minimum of Gibbs free energy.⁹ The calculations were carried out between 800 °C and 1600 °C at 1 atm. Different amounts of Al were used so that the

influence of the amount of aluminium on corrosion could be determined. The mol ratio of hBN to TiB_2 used was 6.58–3.42. The sum of hBN and TiB_2 was 10 mol.

For all calculations any possibly nitrides, borides and metals as well as all gas species were taken into account. The compounds in the gas phase with the highest concentrations of each component are plotted in the diagrams only. These species are the ones which are predominantly responsible for the evaporation. The liquid metal was modelled in the program using a simple substitutional solution approach based on the Redlich–Kister–Muggianu polynomial expression.

3. Results and discussion

3.1. Microstructural analysis

After application tests the surface of the boat showed a relatively deep groove in the centre (Fig. 1b) where the metal wire was applied during evaporation to feed the boat with aluminium. The shape of the groove indicated that this could be mainly connected with mechanical wear due to the Al wire, but temperature differences could intensify local corrosion. A cross section through the interface near the groove was prepared using the ion beam technique (Fig. 3a and b). The micrographs revealed a 100- to 250- μm thick metal layer including grains up to 30 μm in size. EDX analysis of these particles showed that they were AlN precipitates. Small fragments of hBN were also visible inside the metal layer. Very few TiB_2 particles remained (not shown in the micrographs). The cross sections revealed that the dissolution rates of hBN and TiB_2 were quite similar.

No Ti was found in the remaining Al between the AlN particles by EDX analysis. However, more detailed analysis of the interface clearly revealed the dissolution of the TiB_2 (Fig. 3b) grains. The surfaces of the hBN grains were covered by AlN layers, indicating the passivation of hBN by formation of AlN (Fig. 3b). In addition the small crevasses between the hBN lamellas (Fig. 4) were found to contain Al. In these areas, besides AlN, Al_2O_3 and calcium aluminates were detected by EDX. The aluminates were most probably formed by the reaction of Al with B_2O_3 and the calcium borates existing in the boats. Small TiN precipitates were also found in the Al/AlN precipitates (Fig. 4). This indicates that TiN formed during manufacture did not dissolve in Al as quickly as the other components did. XRD analysis of the surface at the centre of the boat revealed AlN and Al to be the main phases. Small amounts of TiB_2 and hBN could also be detected.

AlN, TiB_2 , some Al and $\text{Ti}_3\text{Al}_2\text{N}$, TiAl_x , $\text{TiC}_x\text{N}_y\text{O}_z$ ($x + y + z < 1$) and hBN were detected in the cooler area of the surface near the clamps of the boat. This indicates that higher Ti concentrations existed in these areas.

SEM analysis of the surface mainly showed Al crystals in different shapes (Fig. 5a and b). In addition, small amounts of nitrogen were found in nearly all areas and oxygen was observed in a few areas. The surface also exhibited some cracks due to the different thermal expansion behaviours of the aluminium and

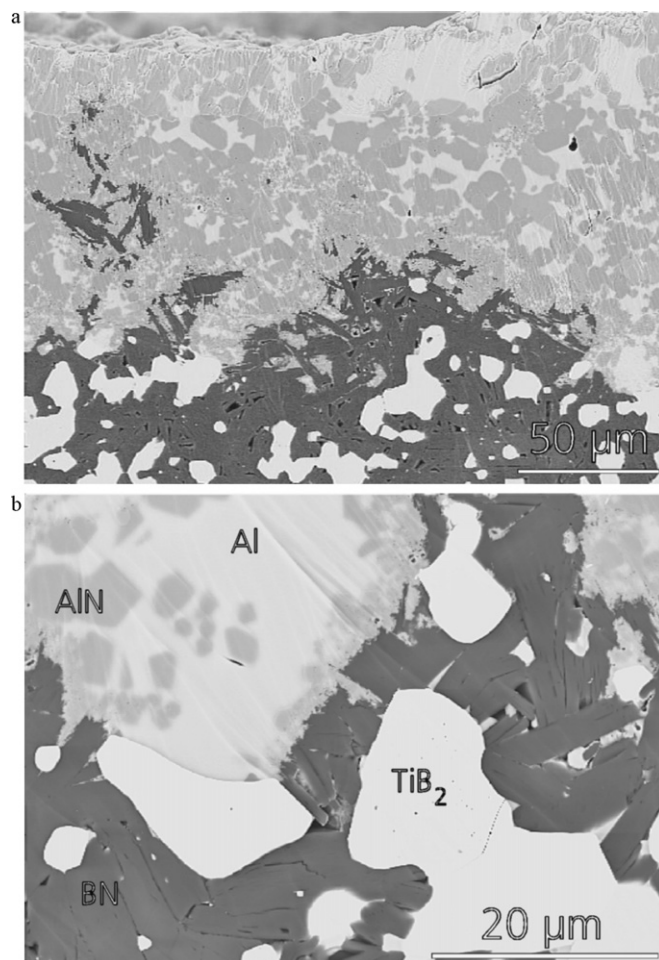


Fig. 3. FESEM micrograph of the cross section of the hBN/ TiB_2 two-component evaporation boat after aluminium evaporation for 8 h: (a) overall view and (b) detail of the interface between metal and evaporation boat with phases marked (based on EDX measurements).

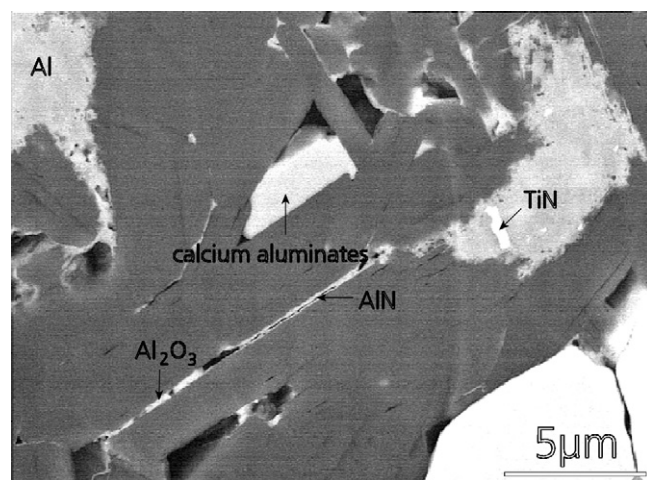


Fig. 4. FESEM micrograph and EDX results of the hBN/ TiB_2 two-component evaporation boat below the Al-ceramic interface after aluminium evaporation for 8 h.

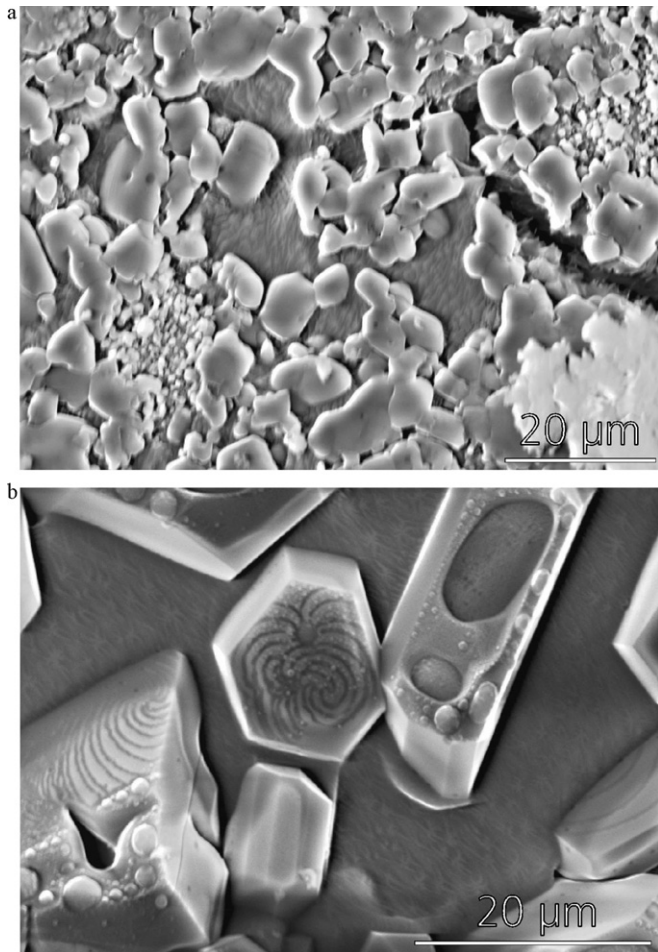


Fig. 5. SEM micrographs of the surface after aluminium evaporation for 8 h: (a) in the hot area and (b) in the colder area closer to the clamps.

the evaporation boat. The crystals in the centre and in the cooler regions differed slightly in shape (Fig. 5a and b).

3.2. Thermodynamic calculations and discussion of the corrosion mechanism

Thermodynamic calculations were carried out for the interpretation of the results of the SEM investigations using the FACTSAGE program. The starting composition was 6.58 mol hBN and 3.42 mol TiB_2 and between 10 mol and 300 mol aluminium. The hBN/ TiB_2 mol ratio corresponded to a volume ratio of 60/40. The calculation results demonstrate that the hBN is thermodynamically unstable and therefore reacts with Al to form AlN over the entire temperature region. According to the results, the products of the reaction between hBN and Al below 1000 °C are AlN as well as a small amount of AlB_2 which decomposes above 1050 °C. At higher temperatures only the aluminium melt, AlN and TiB_2 are in equilibrium for a large excess of Al. For an amount of 10 mol% Al, small amounts of AlB_{12} (0.5 mol) are also found due to the low solubility of boron in the aluminium melt. The boron dissolved in the liquid melt reaches values of up to 10 wt% at 1600 °C (Fig. 6). The solubility of the titanium and chemically dissolved nitrogen in the Al melt is very

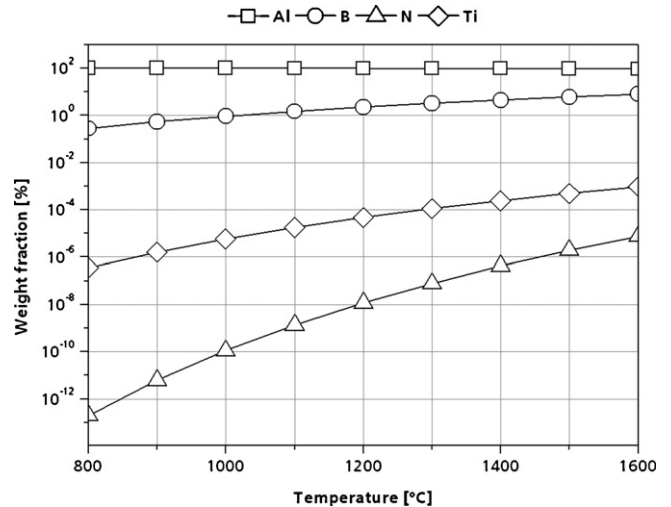


Fig. 6. Calculated composition of the melt as a function of temperature (10 mol Al to 300 mol Al was used in the calculations and give the same results).

low. At 1600 °C in the calculation with an excess of 300 mol aluminium (approximately 8 kg) only 2.5% of the initial TiB_2 amount dissolved in the liquid (Fig. 7). Based on thermodynamic considerations TiB_2 must therefore be stable. This contradicts the microstructural observations which suggested that the dissolution rate of hBN and TiB_2 was very similar (Fig. 3). This is most probably caused by the strong reduction in the hBN dissolution rate due to the formation of a passivating AlN-layer.

If the passivation of hBN by AlN is taken into account and only the solubility of AlN and TiB_2 in an aluminium melt is calculated, the weight fraction of Ti in the liquid is 6×10^{-3} wt% and is only slightly higher than the concentration determined through calculation of the solution of hBN and TiB_2 (1×10^{-3} wt%) at 1600 °C. The solubility of B in the melt is lower in the case of AlN/ TiB_2 interaction with aluminium than in the case of hBN/ TiB_2 interaction with the melt. These results agree with the Al–B–Ti phase diagram¹⁰ indicating a solubil-

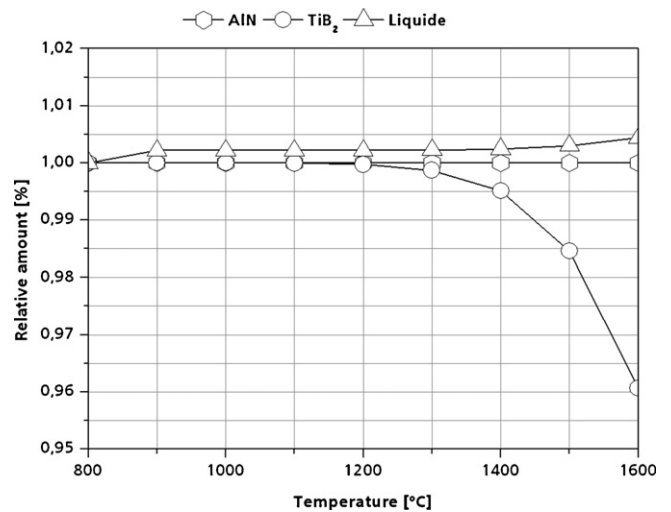


Fig. 7. Calculated relative amounts of the condensed phases as a function of temperature (300 mol Al was used in the calculations to show the effect more pronouncedly).

ity of approximately 0.05 at.% Ti at 1300 °C for TiB₂ (Fig. 9). The solubility decreases greatly with an excess of boron and increases with a deficit of boron.

EDX analysis of the remaining metal in the cross section gave no evidence of Ti dissolved in the aluminium or of separate AlTi_x-phases in the hot region of the evaporator. This experimental evidence also supported the results of the thermodynamic calculations. Therefore the titanium solubility cannot explain the observed dissolution of the TiB₂ in the aluminium melt during evaporation of Al. A possible mechanism could instead be evaporation of Ti together with Al. The evaporation rate (*R*) per unit area can be estimated using the Knutsen evaporation mechanism:

$$R = \frac{pN_A}{\sqrt{2\pi MRT}}$$

where *p* is the partial pressure, *N_A* Avogadro's number and *M* the molar weight. In Fig. 8 the logarithm of the partial pressures of the different species in the gas phase are given. The partial pressure of Ti is nine orders of magnitude lower than that of Al (Fig. 8). Hence, the evaporation rate of Ti is also 10⁹ times lower than that of Al. The evaporation of 100 kg aluminium will be accompanied by the evaporation of less than a mg titanium.

Even if the fact that boron could evaporate faster, thus resulting in an increase in the solubility of Ti in the melt, were taken into account, the extent of evaporation of Ti would still be quite low. Therefore the evaporation rate of titanium cannot completely explain the observed dissolution of TiB₂ either. A possible additional mechanism could be transport of titanium through the melt due to the high thermal gradient within the evaporation boat (the ends of the clamps were at a temperature of less than 600 °C). Strong concentration gradients arise in the melt (Fig. 7). The Ti concentration in the melt is nearly 1 × 10⁻³ wt% at 1600 °C, but only 10⁻⁷ wt% at 800 °C. This gradient is responsible for transport of Ti to the colder melt regions where it crystallises or reacts with other components. This is also in agreement with the microstructural observations indicating that more Ti was found in the colder parts. Addition-

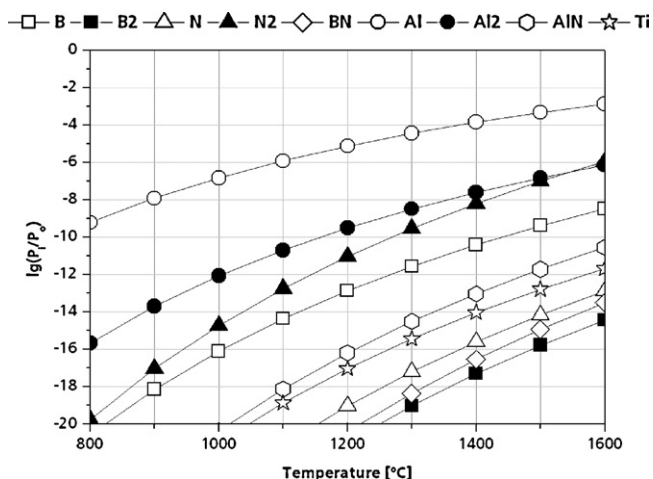


Fig. 8. Calculated composition of the gas phase as a function of temperature (10 mol to 300 mol was used in the calculations).

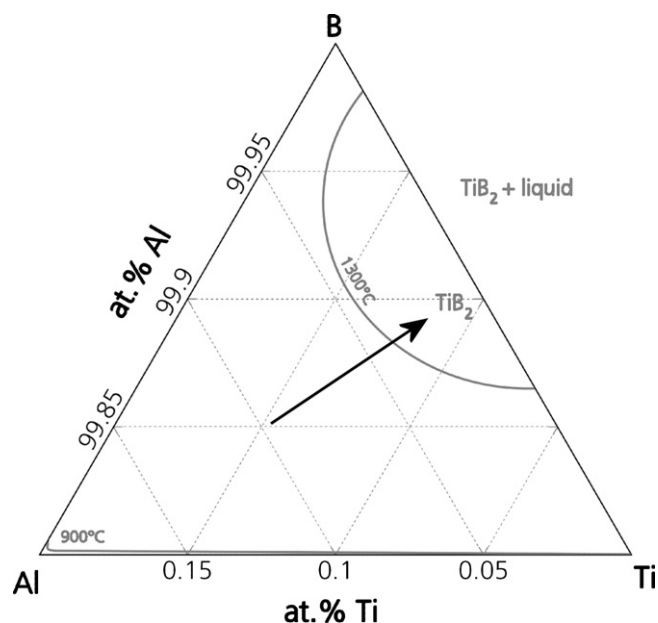
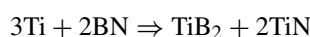
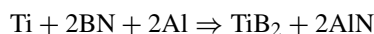


Fig. 9. Liquidus projection of the Al rich corner of the Al–B–Ti phase diagram at 900 °C and 1300 °C (data by ¹⁰). The arrow points into the direction of the TiB₂ composition.

ally the dissolved Ti will be consumed in the cold area by the reaction with hBN forming TiB₂ according for examples to the reactions



or by the crystallisation of different phases from the melt.

The observed formation of Ti₃Al₂N, TiAl_x and TiC_xN_yO_z in this zone is also in agreement with the calculation results.

The calculations of the interaction of the calcium borates or B₂O₃ with an excess of Al indicate the formation of Al₂O₃ or calcium aluminates and the dissolution of boron in the aluminium. The oxide grain boundary phases in the evaporation boats hence also react with aluminium and are not stable during application. This is in agreement with the detection of Al₂O₃ and calcium aluminates near the interface (Fig. 4).

The thermodynamic calculation predicts that the addition of AlN to the hBN/TiB₂ two-component evaporation boats will not change the stability primarily due to in situ formation of AlN in the two-component evaporation boats during application. But the addition of AlN can influence the stability by kinetic reasons. Analysis of the corroded cross section showed the formation of AlN passivating layers in agreement with the thermodynamic calculations. On the other hand, large AlN crystals were found in the liquid aluminium. This indicates that there was a certain solubility of AlN in the melt. Compositional analysis of the gas phase revealed that, besides Al, nitrogen evaporated (partial pressure 100 times lower than that of Al). This indicates that the AlN also decomposes slowly into Al and gaseous nitrogen. Therefore, the addition of AlN to two-component evaporation boats could lower the extent of dissolution of the thin passivating AlN

layers and therefore improve the stability during application. If this additional AlN has an influence on the stability cannot be predicted by thermodynamics, but strongly depends on the kinetics of dissolution of AlN and therefore of the conditions of application. Therefore, the three-component boats show better performance than the two-component evaporator boats in some applications, but not in other applications.

4. Conclusions

Investigations of a two-component hBN/TiB₂ evaporation boat after use for the evaporation of Al and thermodynamic calculations reveal the following:

- hBN is not thermodynamically stable under the application conditions, but will be stabilised by the formation of AlN surface layers in contact with the liquid aluminium.
- Despite the high thermodynamic stability and the resulting low solubility of TiB₂ in the aluminium melt, dissolution of TiB₂ takes place. The dissolution rate is similar to that of hBN due to the absence of the formation of a protective layer. The dissolved titanium mostly precipitates at the colder ends of the evaporation boat in the form of mixed TiAl nitrides, oxynitride, intermetallides and TiB₂.
- In addition, the borate grain boundaries are not stable in contact with the aluminium melt and transform into Al₂O₃ and aluminates.

Acknowledgement

The authors would like to thank ESK Ceramics GmbH & Co. KG for financial support of this research work.

References

1. Griehl S, Müller T, Winkler R. High productive vacuum metallizing of plastic materials with film thicknesses thicker than 10 µm. *Surf Coat Technol* 2003;**169–170**:24–6.
2. DE1280019, Union Carbide Corp.; 1961.
3. US3058809, Carborundum Company; 1962.
4. GB978734, Union Carbide Corp.; 1964.
5. DE1289712, ESK GmbH; 1966.
6. Hauffe W, Obenaus P, Herrmann M, Hapke J. Using the ion-beam slope cutting technique for the examination of the microstructure of composite ceramics with extremely different components (BN/TiB₂) in the scanning-electron-microscope. *Prakt Metallogr* 2004;**41**(7): 343–52.
7. Höhn S, Obenaus P, Hohlfeld J, Lies C. Phasencharakterisierung von Pulverpresslingen für Metallschäume mit dem Ionenstrahlpräparationsverfahren. *Prakt Metallogr Sonderband* 2007;**39**:161–6.
8. Bale CW, Chartrand P, Degterov SA, Eriksson G, Hack K, Ben Mahfoud R, Melancon J, Pelton AD, Petersen S. FactSage thermochemical software and databases. *Calphad* 2002;**26**:189–228.
9. SGPS—SGTE Pure Substances Database. Europe: Scientific Group Thermodata; 2000.
10. Hayes FH, Lukas HL. The Al–B–Ti system (aluminium–boron–titanium). *J Phase Equilib* 1991;**12**(5):609–11.