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Wetting behavior of Si-13.5B alloy on polycrystalline h-BN-based substrates

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Abstract

In this work, for the first time the results of an experimental evaluation of the high temperature behavior of molten Si-B alloy in contact with refractory materials at temperatures up to 1750°C, under static argon atmosphere (p = 850–900 mbar), is shown. The material investigated, having a nominal chemical composition of Si-13.5B (at. %), was fabricated by using the crucible-less electric arc-melting process assisted by the levitation drop method. The wettability of the molten alloy in contact with commercial hexagonal boron nitride (h-BN) substrates was evaluated by means of especially developed sessile drop technique combined with a contact heating procedure. It was found that both couples show a lack of wettability in the whole tested temperature range (the measured contact angle was θ > 130°). The more stable behavior in contact with molten Si-13.B alloy, evidenced by higher θ values and a lack of drop vibration during the high temperature exposition, was observed for the h-BN based composite substrate.

Keywords: silicon-boron alloys, hexagonal boron nitride, wettability, interfaces, AMADEUS Project

1. Introduction

Silicon and silicon-boron alloys have been very recently recognized as excellent phase change materials (PCMs) for applications in ultra-high temperature latent heat thermal energy storage (UHT LHTES) systems [1,2]. Extremely high latent heat values and high melting points of both B and Si have been assumed as the main principles of the European Commission founded AMADEUS Project [3], whose accomplishment should allow overcoming the currently existing limitations of molten salt-based LHTES systems. An implementation of these materials should guarantee obtaining very high energy densities (over 1 kWh/l) two times higher than that of Li-ion batteries and 10-times higher than of molten salts-based counterparts. Nevertheless, a successful finalization of the Project goals requires a proper selection of refractories to build a container for storing molten Si and Si-B alloys at temperatures higher than 1400°C. However, due to a very high reactivity of molten Si and currently not yet recognized behavior of Si-B alloys, this task appears to be very challenging.

It should be noted that in most of the metal/ceramic systems, good wettability is usually assisted by high reactivity, what in turn results in a gradual degradation of metal/ceramic interfaces and related composites. Thus, the following conditions for a strategic selection of refractories should be fulfilled in order to ensure a safe and longtime service of the final LHTES device [4]:

– a low reactivity to avoid contamination of the material, and thus also a non-wetting behavior (the contact angles much higher than 90º) in contact with a molten material to increase the container lifetime.

The non-wetting behavior is observed in some non-reactive metal/ceramic systems [4], however in the case of Si (and probably Si-based alloys), the situation is completely different and more complicated. The high chemical affinity of Si to oxygen, nitrogen and carbon makes it highly reactive and wettable in contact with almost all ceramic materials. Among the refractories, the only one reported exception is hexagonal boron nitride (h-BN) [5] that shows non-wetting behavior with molten Si at temperatures close to its melting point. This feature of h-BN makes it as an “ideal” candidate to contain molten material in LHTES systems. The Si/h-BN system

contact angle values reported at temperatures higher than 1500°C, are very scarce. The only one experimental result at temperatures up to 1750°C, is reported in our recent work [6]. On the other hand, Si-B alloys/h-BN couples have not been examined at all. Therefore, the main purpose of the present work is to experimentally examine the wetting behavior of the abovementioned Si-B alloy in contact with commercially available h-BN substrates at temperatures up to 1750°C, by using the sessile drop method.

2. Materials and methods

The following materials were used in this work:

1. the Si-B alloy, with a nominal chemical composition of Si-13.5 B (at. %), was fabricated by the crucible less electric arc melting method, at Leibnitz Institute for Solid State and Materials Research Laboratory (Dresden, Germany). The nominal composition of the alloy was selected as hypereutectic (based on Si-B binary phase diagram [8], due to a predicted beneficial effect of such composition on increasing the latent heat value [9]. The Si-13.5B alloy samples (Fig. 1), with a mass varying between 0.2 and 0.6 g, were produced from low purity batch materials (Si: 99.99%; B: 99.9% – provided by Onyxmet, Poland).

2. commercially available h-BN based sintered substrates:

   – Henze HeBoSint® D100 – pure h-BN sintered without using binders;

   – Henze HeBoSint® O120 – (h-BN + SiC + ZrO_2) composite sintered without using binders.

Fig. 1. An example of Si-13.5B alloy sample fabricated by crucible less electric arc melting method, at Leibnitz Institute for Solid State and Materials Research (Dresden, Germany)

Before experiments, the contacting surfaces of h-BN substrates in as-received states were cut on plates with a diameter of ∅17 mm and a height of 4 mm, by the Struers Accutom-100 metallographic cutter. The contacting surfaces of h-BN substrates before tests were subjected to a gentle mechanical polishing on a piece of office paper in order to obtain the initial surface roughness of r_a ~150 nm (the surface profile was measured by NT-MDT NTEGRA Spectra Scanning Probe Microscope). The Si-13.5B alloy samples were ultrasonically cleaned with isopropanol and dried.

Wetting tests of Si-13.5B/h-BN couples (Fig. 2a) have been carried out by a sessile drop method combined with a contact heating procedure. The experimental complex (described elsewhere [7]) for examining high temperature capillarity phenomena was used to examine 2 couples i.e. **couple A**: Si-13.5B/h-BN and **couple B**: Si-13.5B/(h-BN + SiC + ZrO_2) in one single test ("2 in 1" testing procedure); in accordance to the temperature profile shown in Figure 2b. Five intervals at 1450°C/5 min, 1550°C/5 min, 1650°C/5 min, 1700°C/5 min and 1750°C/10 min under static argon atmosphere (p = 850–900 mbar), were applied. The acquired images were used for computation of the contact angle θ values by using ASTRA2 (IENI-CNR, Italy [10]) special software, as well as for preparing a real-time movie from the high temperature test.

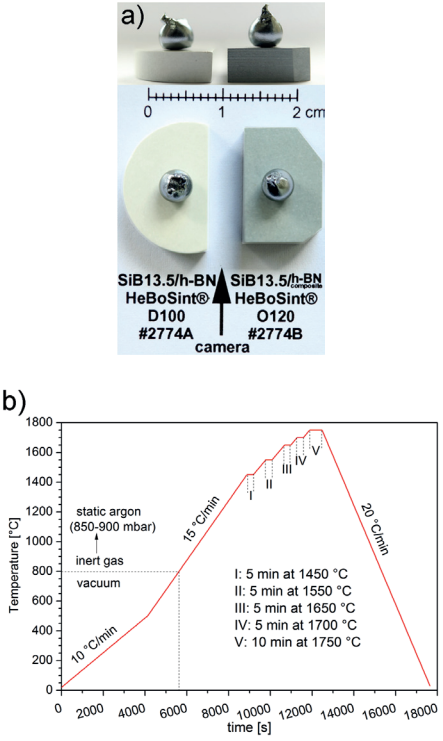

Fig. 2. A macroview of the couple A (Si-13.5B/h-BN) and couple B (Si-13.5B/(h-BN + SiC + ZrO_2)) composite before the sessile drop test (a). The heating/cooling scheme (a temperature profile) used upon the wettability test following the "2 in 1" procedure (b)

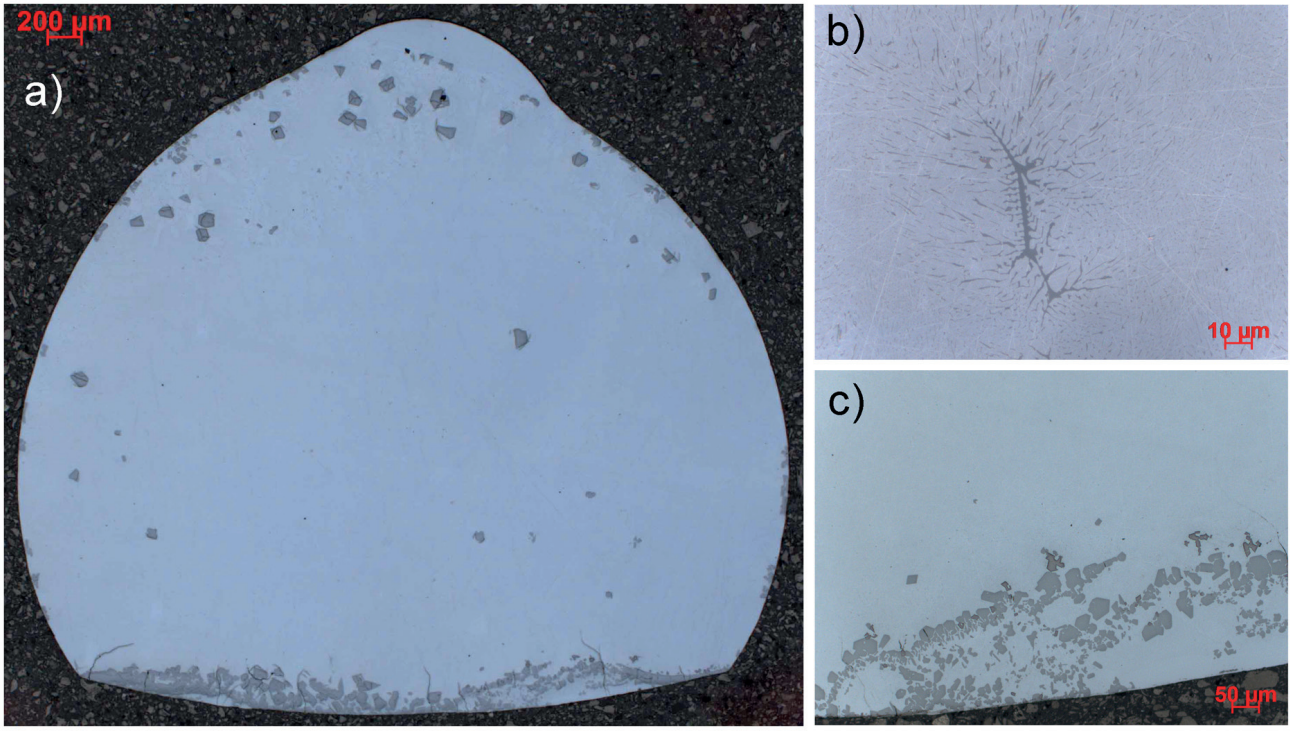

Fig. 3. Light microscopy images of the cross-sectioned Si-13.5B alloy in the as-fabricated state by using the electric arc melting method: the whole drop (a), (Si + SiB_3) eutectic (b); particles at the bottom of the drop (c)

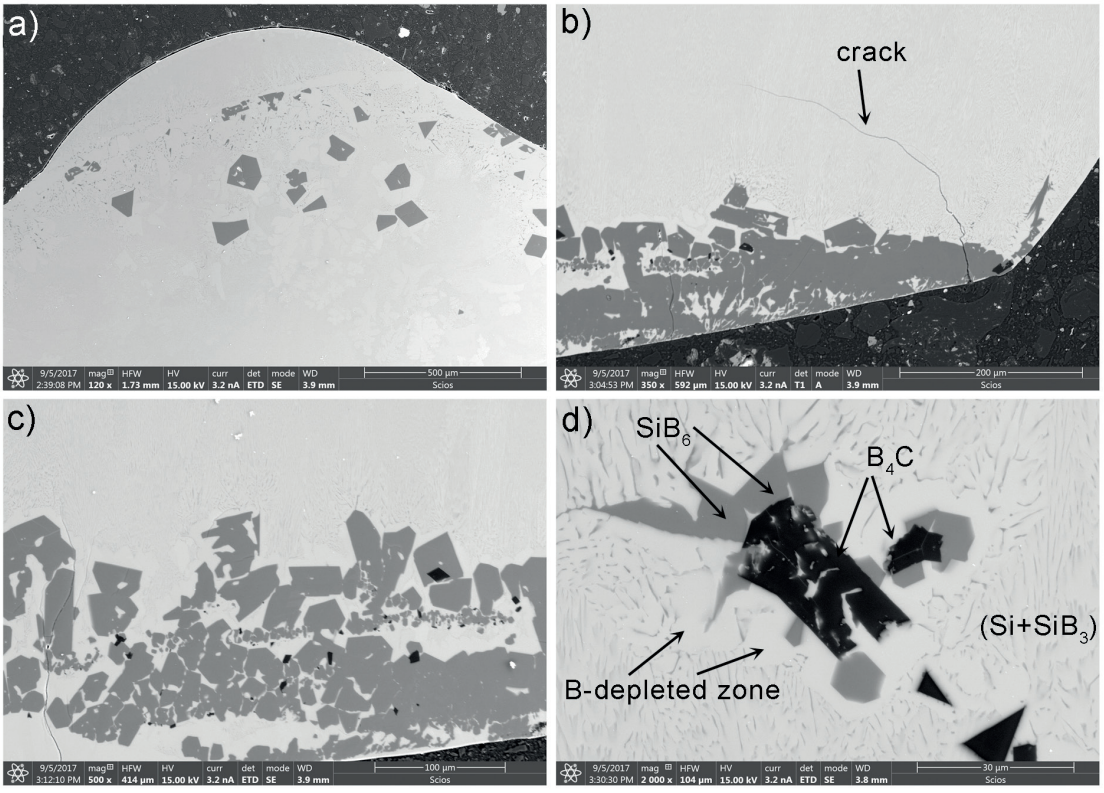

Fig. 4. The FEG SEM images of the cross-sectioned Si-13.5B alloy in the as-fabricated state by using the electric arc melting method: the top part of the drop (a), the bottom of the drop (b,c). The EDS estimated phase composition of the alloy (d)

The microstructure and chemistry of the Si-13.5B alloy in its as-produced state was characterized by means of Carl Zeiss Axio Observer ZM10 light microscopy and by FEI SciosTM field emission gun scanning electron microscopy (FEG SEM) coupled with energy dispersive X-ray spectrometer (EDS). The Si-13.5B alloy piece was cross-sectioned by Struers Accuttom P-100 precise metallographic cutter and then metallographically polished by mechanical grinding with SiC papers and diamond pastes (3 and 1 μm).

3. Results and discussion

3.1. The Si-13.5B alloy in as-received state

It was found that the Si-13.5B alloy in the as fabricated state (before the wettability tests) is characterized by a non-uniform microstructure (Fig. 3a). The interior of the Si-13.5B drop is quite homogeneous and consists of a Si matrix and Si + SiB_3 eutectic (Fig. 3b). On the other hand, the presence of at least two types of crystals located mostly near the surface drop, is also documented (Fig. 3c). Furthermore, cracking on the bottom part is also observed. The results of a more detailed FEG SEM/EDS structure characterization (Figs. 4a–d) allows recognizing fine dark particles of boron carbide (B_4C) phase, and the brighter ones as the SiB_6 phase (Fig. 4d). While the existence of SiB_6 crystals is consistent with the nominal chemical composition and the Si-B binary phase diagram [8], the presence of relatively lower fraction of B_4C particles should be justified in terms of the carbon contamination of batch materials. Nevertheless, precise chemical analyses, e.g. by ICP-MS method, are needed to determine the exact composition of the fabricated Si-13.5B alloy.

3.2. The wettability kinetics

In Figure 5, the image showing a comparison between the Si-13.5B/h-BN couples before and after the wettability test is shown. The visual inspection revealed: (I) a color changeover of the pure h-BN (Henze HeBo Sint® D100) substrate (from white to yellowish); (II) the formation of dark zones on both h-BN based substrates in close vicinity to the solidified drops. Nevertheless, more detailed research on reactivity in these couples will be carried out in future.

In Figure 6, the images *in-situ* recorded by the high speed camera during the test are presented. The wettability kinetics is expressed as the plots of contact angle θ value vs. exposure time (in accordance to the preassumed temperature profile of the test) (Fig. 7). The contact angle was measured after complete melting (after the full-drop formation) in solid/liquid/vapour triple points on the left and right sides of each drop.

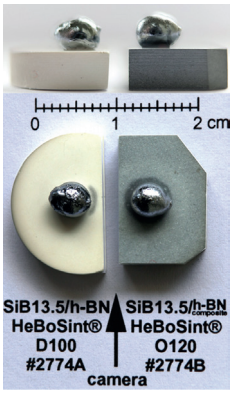

Fig. 5. A macroview of the couple A: Si-13.5B/h-BN and couple B: Si-13.5B/(h-BN + SiC + ZrO_2) composite after the sessile drop test performed by "2 in 1" testing procedure

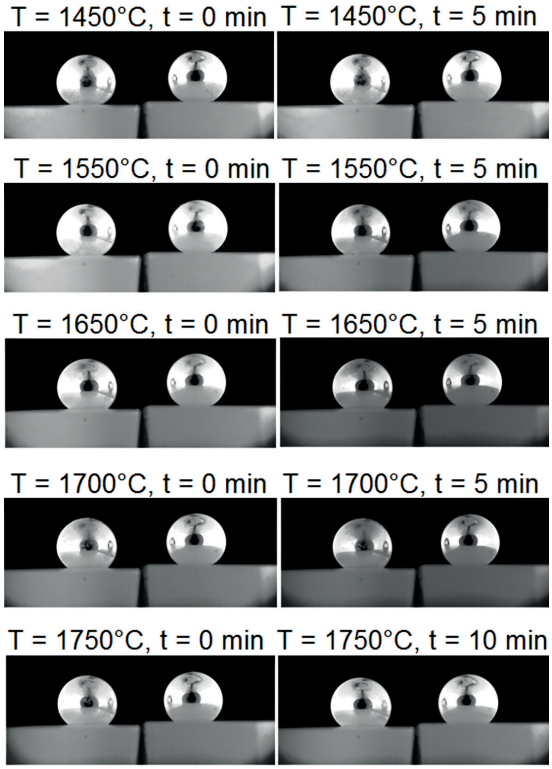

Fig. 6. Images in-situ recorded by the high speed camera during the wettability test at the start and end of each temperature interval. The Si-13.5B/h-BN couple is on the left, while the Si-13.5B/(h-BN + SiC + ZrO_2 composite) is on the right

It should be noted that both couples show a non-wetting behavior in the whole tested temperature range, i.e. the measured contact angle θ values were much higher than 90°. However, some differences might be found between the performance of "pure" h-BN substrate (Henze HeBoSint® D100) and that of the h-BN based composite (Henze HeBoSint® O120). The Si-13.5B/pure h-BN couple (Fig. 7a) exhibited θ =

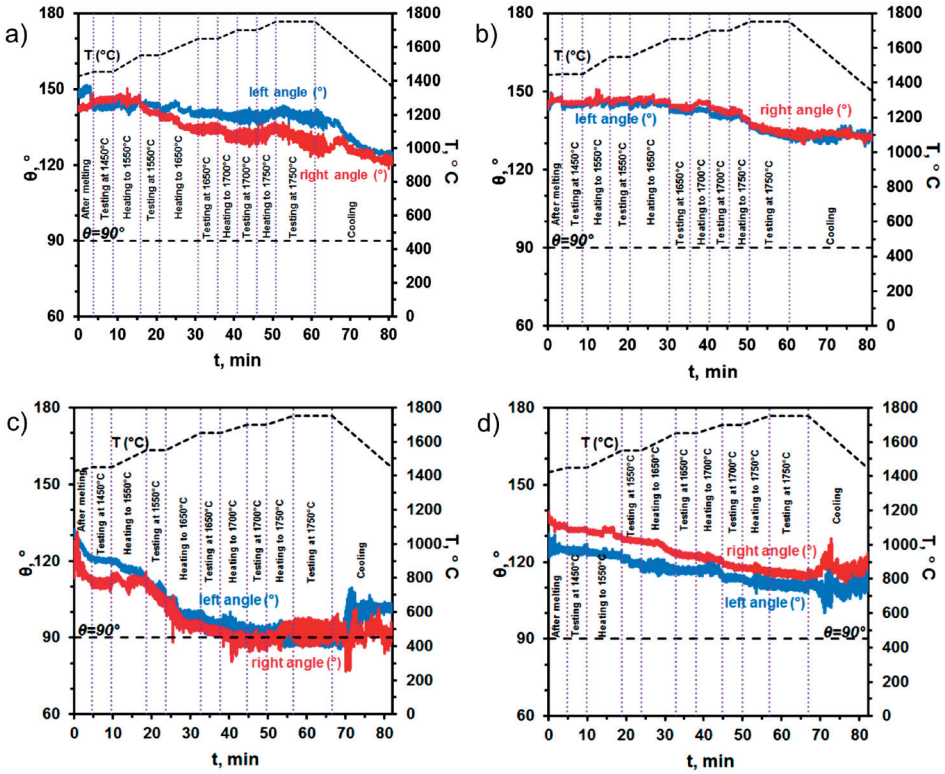

Fig. 7. Wetting kinetics curves calculated for the couple A: Si-13.5B/h-BN (a) and couple B: Si-13.5B/(h-BN + SiC + ZrO_2 composite) (b) couples tested by the sessile drop method at temperatures up to 1750°C. The Si/h-BN (c) and Si/h-BN + SiC + ZrO_2 composite) (d) couples examined under the same testing conditions, were used as the reference (based on [6])

140−145° with raising temperature up to 1550°C, after that a gradual decrease of θ took place (to θ ~130°) upon testing at higher temperatures. The behaviour was quite different for the other couple. The Si-13.5B/(h-BN + SiC + ZrO_2) couple exhibited much more stable behavior – the contact angle of θ ~145° did not change during the test up to 1700°C. Only after testing at the highest temperature (1750°C), a decrease down to θ ~135°, was recorded. Furthermore, a relatively large scatter of θ measured on the left and right sides of the Si-13.5B/h-BN couple (Fig. 7a) should be associated with drop vibration (oscillations revealed at the triple line). The drop vibration effect was previously observed in many systems (e.g. Si/Al_2O_3 [11]) and it was related to the effect of a partial substrate dissolution followed by a gaseous product formation and then released. In the present case of the Si/h-BN system, it is reasonable to assume that a slight dissolution of the substrate takes place and the dissolved nitrogen is released through the liquid/vapor interface as N_2. Under such assumption, it should be noted that the lack of drop vibration in the Si-13.5B/(h-BN + SiC + ZrO_2) couple proves that the substrate dissolution was somehow suppressed. Nevertheless, this finding as well as the role of SiC and ZrO_2 additions will be clarified by a detailed structural characterization of interfacial areas of both couples in future experiments. Finally, by comparing the results of presently examined Si-13.5B alloy (Fig. 7a,b) to the behavior of pure silicon on the h-BN substrates (previously [6] examined under the same condition as in the present work) (Fig. 7c,d), it might be also concluded that the addition of boron decreases the reactivity in the system. This statement is in line with our previous conclusions that the reactivity mechanism in Si/h-BN is mostly controlled by the dissolution of h-BN substrate. Thus, in the view of these findings, it is also reasonable to conclude that the addition of boron simply decreases the dissolution of boron nitride.

4. Conclusions

The Si-13.B alloy was successfully fabricated from low purity elements by using the electric arc melting technique. The alloy was for the first time subjected to an ultrahigh temperature (up to 1750°C) wettability test by the sessile drop method. Two types of commercial refractories were selected as the substrates: the “pure” h-BN and the h-BN based composite. It was found that both couples show a lack of wettability in the whole tested temperature range (the measured contact angle was θ > 130°). The more stable behavior in contact with molten Si-13.B alloy, reflected by higher θ values and a lack of drop vibration during high temperature exposition, was observed for the h-BN based composite substrate. Regarding predicted applications in LHTES

systems, both refractories might be considered as possible candidates for container materials. However, before that both interfacial phenomena and thermal cycling behavior need to be experimentally evaluated.

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