Silicon-Boron Alloys as New Ultra-High Temperature Phase-Change Materials: Solid/Liquid State Interaction with the h-BN Composite

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Abstract

Silicon-boron alloys have been recently pointed out as novel ultra-high temperature phase change materials for applications in Latent Heat Thermal Energy Storage (LHTES) and conversion systems. One of the emerging challenges related to the development of such devices is a selection of refractories applicable to build a vessel for storing molten Si-B alloys at high temperatures and under consecutive melting/solidification conditions. Previously, it has been documented that hexagonal boron nitride (h-BN) is the only one ceramic showing a non-wettability and limited reactivity with Si-B alloys at temperatures up to 1750 °C, what makes it a good candidate of the first selection for the predicted application. Nevertheless, pure h-BN shows a rather low mechanical strength that could affect a durability of the LHTES vessel. Therefore, the main purpose of this work was to examine high temperature behavior of commercial high strength h-BN composite having a nominal composition of h-BN-24ZrO₂-6SiC (vol.%) in contact with a solid/liquid eutectic Si-3.2B alloy. Two types of sessile drop experiments were carried out: a step-contact heating up to 1750 °C, and a thermocycling at 1300 – 1450 °C composed of 15 cycles of the alloy melting/solidification. The obtained results showed a lack of wettability in the examined system at temperatures up to 1750 °C. The Si-3.2B alloy presented good repeatability of melting/solidification temperatures in consecutive thermal cycles, which was not affected by the interaction with the h-BN composite. However, due to reactions taking place between the composite's components leading to structural degradation, it is not recommended to increase operational temperature of this material above 1450 °C.

Keywords Silicon-boron alloys · Hexagonal boron nitride · Sessile drop method · Latent heat thermal energy storage · AMADEUS project

1 Introduction

Latent Heat Thermal Energy Storage (LHTES) plays an important role as a complementary technology for

renewable energy sources (e.g. concentrated solar power systems) making them available during blackout periods [1, 2]. The heart of every LHTES is a Phase Change Material (PCM) – a substance that is capable of storing and releasing large amounts of energy upon melting and solidification at a certain temperature range. Both organic and inorganic materials are under consideration to be used as PCMs. Regarding high-temperature applications, metals and alloys seem to be reasonable PCM candidates since they exhibit clear advantages over already applied molten salts or eutectic salts mixtures e.g. higher melting points, better thermal diffusivity, heat capacity and energy density. So far, research efforts in this field of using metals as PCMs have been mainly focused around aluminum, magnesium and zinc alloys having melting points $T_m < 700$ °C [3].

The main goal of European Commission founded AMADEUS Project (2017-2019) [4–6] is to combine extremely high latent heat values of silicon (1800 J/g

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at $T_m = 1414\text{ }^{\circ}\text{C}$) and boron (4650 J/g at $T_m = 2076\text{ }^{\circ}\text{C}$) with a very high electrical power density of modern thermophotovoltaic (TPV) converter, in order to develop novel ultra-high temperature LHTES system. It is expected that using silicon and/or silicon-boron alloys as the PCMs should allow prominently increase capabilities of the state-of-the-art molten salt or metal-based LHTES devices, both in terms of operational temperatures and available energy density. Nevertheless, an increase of working temperature of Si-B alloy based LHTES system to $\sim 1400\text{ }^{\circ}\text{C}$ brings a number of new materials science related challenges. One of them is significantly increased chemical reactivity of involved materials at such high temperatures. Consequently, a selection of proper refractories to build the PCM vessel that will ensure long-term reliability during consecutive melting/solidification of Si (or Si-B alloys) becomes a demanding task.

In general, a lack of strong interaction (reflected by a lack of wetting and a low reactivity) between the PCM candidate and contacting ceramic material, is the most important requirement to be considered when choosing a material to build the high-temperature vessel. However, molten silicon has been already recognized as highly reactive towards most of ceramic materials. Due to high chemical affinity to O, N and C, direct contact of molten silicon with oxides, carbides and nitrides results in a reactive formation of interfacial products and a good wetting represented by contact angle values $\theta < 90^{\circ}$ [7, 8].

Recently [9], we have documented that hexagonal boron nitride (h-BN) is the only one ceramic showing a non-wetting behavior ($\theta > 90^{\circ}$) with molten Si at temperatures up to $1650\text{ }^{\circ}\text{C}$, while the involved interaction is based on a dissolution/precipitation mechanism without a formation of any continuous product layers at the Si/h-BN interface. This behavior was subsequently confirmed in thermocycling experiments at a temperature interval of $1300 - 1450\text{ }^{\circ}\text{C}$ including 15 consecutive cycles of melting/solidification [10]. Moreover, we also found, that the addition of boron to silicon (i.e. using silicon-boron alloys instead of pure Si) further reduces the wettability with h-BN ceramic [9, 10]. Due to a suppressed dissolution of h-BN in Si-B melt, near eutectic Si-B binary alloys exhibit very high contact angles ($\theta \sim 1400\text{ }^{\circ}\text{C}$) at temperatures as high as $1750\text{ }^{\circ}\text{C}$.

Nevertheless, despite of the fact that h-BN shows good high temperature thermochemical compatibility with both silicon and silicon-boron alloys, it is characterized by a rather poor mechanical strength. Therefore, in order to enhance durability of the PCM vessel, high strength h-BN composite ought to be also taken into consideration as a candidate refractory material. Among various available h-BN composites, a special attention is paid to these strengthened by ZrO_2 and/or SiC particles.

The results of reported experimental works [12–14] confirmed that introduction of these ceramic reinforcements strongly enhances compressive strength (up to 10 times), fracture toughness, thermal shock resistance and oxidation resistance of the h-BN matrix. The application area of commercially available h-BN+ ZrO_2 +SiC composites includes e.g. components for high-temperature electric furnaces; insulators for plasma-jet furnaces, ion engines and PVD-ARC equipment; mechanical components, pipes and nozzles for liquid metal handling; molten metal and gas sensor components; casting components for precious metals, dental and other special alloys [15].

In our previous work [16], by using sessile drop experiment we have documented that a commercial h-BN-24 ZrO_2 -6SiC composite is much less wetted by molten Si at temperatures up to $1750\text{ }^{\circ}\text{C}$, as compared to the pure h-BN counterpart. On the other hand, the results of structural characterization of solidified Si/h-BN composite couple have revealed that the wetting behavior is affected by the occurrence of chemical reactions between composite's components. These reactions lead to significant changes of microstructure, phase composition and surface morphology of the h-BN-based composite. Thus, in the view of practical applications of involved materials in ultra-high temperature LHTES units, it is important to deeply explore the course of structural and interfacial phenomena in Si-B alloy/(h-BN-24 ZrO_2 -6SiC) system under predicted working conditions. In the present work we continue our research by examining for the first time the Si-3.2B eutectic alloy/(h-BN-24 ZrO_2 -6SiC) system in sessile drop experiments carried out in accordance to step-heating or thermocycling procedures. In this regard, our previous works on Si/h-BN [9, 10], Si-B/h-BN [11] and Si/h-BN-24 ZrO_2 -6SiC [16] systems tested under the same conditions are treated as direct references. In order to avoid repeating certain information, more details on applied materials and testing procedures are available in our previous works and referenced in proper places in manuscript. This study is a step towards enhancing our understanding of reactivity and wettability of the molten eutectic Si-B alloy with the h-BN ceramic composite, and the performance of both materials under consecutive solid $\leftrightarrow$ liquid phase changes.

2 Materials and Methods

The materials investigated were eutectic Si-3.2B (wt%) binary alloy produced by electric arc melting method (details on applied process are shown elsewhere [11]) and the commercially available hot-sintered h-BN-24 ZrO_2 -6SiC composite (Henze HeBoSint O120, Germany). The Si-3.2B alloy was produced from polycrystalline pure materials (Si: 99.999%; B: 99.9% as provided by Onyxmet,

Poland). The Si-3.2B alloy/(h-BN-24ZrO₂-6SiC) couples were subjected to sessile drop experiments performed by using experimental complex for investigation of high temperature capillarity phenomena, described elsewhere [17]. We used two types of sessile drop experiments (Fig. 1) to investigate performance properties of the selected PCM/refractory materials under an application determined conditions. The first one was designed to have a response about a maximum working temperature that could be applied for the Si-3.2B/(h-BN-24ZrO₂-6SiC) couple placed in the heart of LHTES system. It is worth to emphasize that from the energy density point of view, the higher operational temperature could be achieved, the higher "energy efficiency" is received (i.e. the latent heat released at the melting point could be additionally enhanced by a sensible heat coming from an overheating of the melt). The step-heating experiment included 5 intervals at 1450 °C/5 min, 1550 °C/5 min, 1650 °C/5 min, 1700 °C/5 min and 1750 °C/10 min (Fig. 1a). The main purpose of this

Fig. 1 Temperature profiles of high temperature sessile drop experiments of the Si-3.2B alloy/h-BN composite couples carried out by: a step-heating up to 1750 °C with five intervals (a); a thermocycling including 15 heating/cooling cycles between 1300 and 1450 °C with the intermediate cooling to room temperature after 10th cycle

test was to examine the effect of testing temperature on wetting characteristics, and to establish applicability limits of selected materials. The same temperature profile was applied in our previous works [9, 11, 16]. The second type of the sessile drop test (Fig. 1b) was performed in order to assess the performance of a system upon cycling melting/solidification processes. For this reason, the selected PCM candidate/h-BN composite couple was subjected to a sessile drop experiment containing 15 cycles of heating/cooling between 1300 – 1450 °C, with an intermediate cooling down to room temperature after 10 cycles. The upper and lower temperature limits were selected in order to cover melting and solidification ranges of the Si-3.2B alloy. According to the Si-B binary phase diagram a theoretical melting point of the eutectic alloy is $T_m = 1385$ °C. However, by taking into account the overcooling effect the lower temperature limit was set at $T = 1300$ °C. The heating/cooling rates used upon the thermocycling experiment were relatively higher than that predicted in the final application, in order to examine the materials' behavior under "forced" conditions that should accelerate their potential degradation. During these tests, the temperatures of specific events (melting, solidification) as well as contact angle values were recorded. The same thermocyclic procedure was applied also in our previous work [10]. It should be highlighted that during both sessile drop experiments, the same procedure for the preparation of the high temperature chamber was applied as follows. After placing a metal/substrate couple inside the chamber, gases were evacuated using Scroll and turbo-molecular pumps. When a pressure inside the chamber reached the value of about 1×10^{-6} mbar, heating was started following one of the pre-selected temperature profile. At temperature of 800 °C, the inert gas (static argon, $p=850$ -900 mbar) was introduced to the chamber in order to suppress the evaporation of the silicon-boron alloy.

After the high temperature tests, the solidified couples were removed from the chamber and subjected to a structural characterization by using the Carl Zeiss Axio Observer ZM10 Light Microscope (LM) and FEI SciosTM Field Emission Gun Scanning Electron Microscope (FEG SEM) coupled with Energy Dispersive X-Ray Spectroscopy (EDS). The examinations were performed both on cross-sectioned samples. The sessile drop couples were also non-destructively inspected by X-ray Computed Tomography (CT) technique. The GE Phoenix Nanotom M CT device operating under voltage of 100 kV, current of 65 μ A, exposure time of 500 ms and voxel size of 8.0 μ m was used for the acquisition of X-ray images. A digital reconstruction of the scanned object was performed by using Datos—x reconstruction and VGStudio Max 2.0 commercial software.

3 Results and Discussion

3.1 Characterization of Materials Structure in Initial Condition (Before Experiments)

The Si-3.2B alloy produced by electric arc melting method was characterized by a complex multiphase structure (Fig. 2a) with a matrix composed of a mixture of Si(B) solid solution and Si(B)+SiB₃ eutectic. Additionally, a few randomly distributed particles of silicon tetraboride (SiB₄) and boron carbide (B₄C) were also detected based on the results of detailed SEM/EDS analyses. Although it is well known that EDS exhibits a strong limitation in quantifying light elements like carbon and boron, we used it to examine a local chemical composition inside these particles. The results revealed that the B/Si atomic ratio measured in different sites of the grey particles was 4.11 ± 0.13 , while the B/C atomic ratio for the black ones was 4.07 ± 0.09 , thus corresponding to SiB₄ and B₄C phases respectively. Despite of the fact that the SiB₄ is not marked in the widely accepted form of the Si-B binary equilibrium phase diagram [18], its existence has been documented in more recent experimental works, e.g. [19, 20]. Since the SiB₄ phase exhibits a lower thermal stability as compared to SiB₃ and SiB₆ borides, its presence should be justified in terms of strongly non-equilibrium conditions of the solidification during applied arc-melting processing. The existence of boron carbide particles should be associated with a carbon contamination coming from batch materials. Structural characterization of the h-BN-composite substrate shows that the ZrO₂ (bright) and SiC (grey) particles having an irregular shape and size up to $\sim 10 \mu\text{m}$ were homogeneously distributed in the h-BN matrix (Fig. 2b). More details on the investigated materials are shown in our previous works [11, 16].

3.2 Wettability in Si-3.2B Alloy/(h-BN+SiC+ZrO₂) System

3.2.1 The Step-Heating Experiment (up to 1750 °C)

The fast-forward video recorded during the step-heating test is available as the Electronic Supplementary Material 1,

Fig. 2 SEM images showing a microstructure of the investigated materials: the Si-3.2B eutectic alloy (a) and the commercial h-BN-24ZrO₂-6SiC composite (b)

while the wetting kinetics curve (contact angle θ vs. t) calculated from captured images is presented in Fig. 3.

The contact angle values were very high in the whole examined temperature range, but they slightly decreased from $\theta_{1450} = 147^\circ$ to $\theta_{1750} = 134^\circ$, with increasing testing temperature from 1450 to 1750 °C, respectively. What should be noted is that the Si-3.2B alloy shows a lower wettability (reflected by prominently higher contact angles) with the h-BN composite, than the pure silicon examined under the same testing conditions ($\theta_{1450} = 132^\circ$ to $\theta_{1750} = 110^\circ$) [16]. This finding confirms the previously observed effect of boron addition to silicon on suppressing high temperature wettability through hindering a dissolution of h-BN matrix in the molten alloy [11]. Interestingly, the wetting behavior of the Si-3.2B alloy/h-BN composite couple during cooling from 1750 °C is also quite different than that of previously examined Si/h-BN composite couple. As opposite to the pure silicon counterpart, the Si-3.2B alloy showed a lack of “dewetting movement” (i.e. a lack of visible increase of contact angle) upon cooling down from 1750 °C. This finding gives a one more evidence that addition of boron to silicon stabilizes the investigated system and allows achieving thermodynamic equilibrium between the liquid material and the h-BN-based ceramic.

3.2.2 Thermocycling Experiment – Consecutive Melting/Solidification Between 1300 – 1450 °C

The fast-forward video recorded during the thermocycling experiment is available as the Electronic Supplementary Material 2. Figure 4 summarizes results obtained during the thermocycling experiment, i.e. it gives information about cyclic behavior of the Si-3.2B alloy upon contact heating/cooling with the h-BN composite in terms of the wettability (a “stability” of contact angle) and melting/solidification range in each consecutive cycle. A set of real-time images of the Si-3.2B/(h-BN-24ZrO₂-6SiC) substrate taken after 5 min holding at 1450 °C in each thermal cycle, is presented in Fig. 4a, while observed temperatures of specific events (melting, solidification) and contact angle values are shown in Fig. 4b and c,

Fig. 3 The wetting kinetics curve (showing a change of contact angle θ vs. testing time) obtained for Si-3.2B alloy subjected to step-heating up to 1750 °C in contact with the h-BN composite substrate (data for pure Si are taken from ref. [16]). Please note that contact angle values at 1750 °C/5 min were characterized by high uncertainty due to a presence of some solid state particles in the vicinity of triple line

Fig. 4 Images of the Si-3.2B drop/(h-BN-24ZrO₂-6SiC) substrate in-situ recorded after 5 minutes holding at 1450 °C in each cycle (a). The recorded temperature ranges of melting and solidification of the

Si-3.2B alloy (b). The average contact angle θ values calculated for the Si/(h-BN-24ZrO₂-6SiC) couple during consecutive cycles (after 5 min holding at 1450 °C) (c)

respectively. It is documented that the Si-3.2B alloy completely melts at temperature around 1384 ± 8 °C (average from 15 cycles) (Fig. 4b), which is very close to theoretical melting point of eutectic composition ($T_m = 1385$ °C) described by Olesinski and Abbaschian in the Si-B binary phase diagram [18]. During cooling down from 1450 °C at 10 °C/min the full solidification of the Si-3.2B drop was obtained at temperature of 1306 ± 2 °C (average from 15 cycles), thus giving the undercooling of $\Delta T = 78$ °C. This value is slightly higher than that of pure Si ($\Delta T = 70$ °C) previously examined under the same testing conditions [10]. Generally, the melting/solidification behavior of the Si-3.2B alloy was characterized by a good repeatability in consecutive thermal cycles, as well as it seems to be not affected by interaction with the h-BN composite. The average contact angle recorded after 5 min holding at 1450 °C in each consecutive cycles presented very high values, significantly above the non-wetting regime ($\theta > 90^\circ$) (Fig. 4c). Nevertheless, a slight decrease of contact angle from $\theta = 156^\circ$ (recorded in the 1st-5th cycles) to $\theta = 137^\circ$ after the 15th cycle should be related to an in-situ modification of the h-BN composite's surface that took place during the high temperature exposure. It should be noted that this behavior was strikingly different than that observed during testing of pure Si/h-BN couple under the same conditions [10]. In that case, the interaction was dominated by a cyclic dissolution of h-BN ceramic in molten Si at 1450 °C followed by a reprecipitation of h-BN platelets during cooling to 1300 °C.

Consequently, the solid/solid interface of the Si/h-BN couple was gradually modified leading to increase of contact angle in consecutive cycles and a spontaneous detachment of Si drop from the h-BN substrate. A lack of this phenomenon between presently examined materials, confirms that addition of boron to silicon decreases a dissolution of h-BN ceramic in molten alloy, and thus it also hinders the reprecipitation of h-BN platelets during cooling of B-, C- and N-saturated melt.

3.3 Structural Characterization of Si-3.2B Alloy/(h-BN+SiC+ZrO₂) Sessile Drop Couples After High Temperature Tests

A comparison of microscopic images taken from cross-sectioned Si-3.2B alloy/h-BN-24ZrO₂-6SiC couples clearly points towards a very strong impact of testing temperature on the course of involved interfacial phenomena. In the case of the sample subjected to the step-heating experiment at temperatures up to 1750 °C, the results of combined LM and SEM/EDS analyses (Fig. 5) revealed a substantial alteration of materials structure as well as the formation of interfacial products. Based on the results of detailed local EDS chemical composition analyses the following structural features were recognized:

1. a matrix of the alloy composed of the mixture of Si(B) solid solution and (Si+SiB₃) eutectic (Fig. 5b);

Fig. 5 The results of LM and SEM/EDS examinations of the cross-sectioned Si-3.2B alloy/h-BN composite couple after the step-heating experiment up to 1750 °C: a general view of the solidified Si-3.2B alloy (a); a microstructure of solidified drop showing Si+SiB₃ eutectic features (b); two types of silicon borides (SiB₃ and SiB₆) distributed in the close vicinity of drop surface and at the alloy/ceramic interface; c a discontinuous bicomponent product layer (B₄C+SiC) formed at the Si-3.2B alloy/h-BN composite interface (d)

- two types of silicon borides (SiB_3 and SiB_6) (Fig. 5c) in the form of relatively large crystals distributed in the close vicinity of drop surface and the alloy/ceramic interface (a lack of the meta-stable SiB_4 phase observed in the initial material proves that during the ultra high-temperature exposure the alloy changed its structure towards a more equilibrium state);
- a dense, but discontinuous bicomponent product layer formed at the Si-3.2B alloy/h-BN composite interface. The product layer was composed of B_4C and SiC crystals (Fig. 5d).

A large fraction of the ($\text{Si}+\text{SiB}_3$) eutectic mixture in the structure of solidified Si-3.2B drop presents a good agreement with its theoretical equilibrium composition. A distribution of silicon borides at gas/liquid and liquid/solid interfaces of the solidified couple crystals suggests that they were produced during cooling by a nucleation and growth. On the other hand, the interfacial product layer ($\text{B}_4\text{C}+\text{SiC}$) was most probably formed due to the dissolution of h-BN matrix in the molten alloy assisted by a thermal decomposition of primary SiC particles.

Analogously as in our previous experimental work [16], SiC particles embedded in the near surface area of the

h-BN body are decomposed ($\text{SiC} \rightarrow \text{Si} + \text{C}$) in contact with the liquid Si-B alloy. Consequently, "free carbon" is dissolved in the liquid Si-B alloy, while its amount increases with increasing testing temperature. During cooling B- and C- and N- saturated melt down from from 1750 °C, both B_4C and SiC particles are nucleated and grown at the interface on the drop side via a dissolution/precipitation mechanism. In this regard, the main difference between the previously examined pure silicon [16] and presently tested Si-3.2B alloy is the phase composition of the discontinuous interfacial product layer. In the former case it was a single-phase SiC , while addition of boron in the latter one allows producing bicomponent layer made of SiC and B_4C precipitates. Additionally, in order to provide a general view on distribution and morphology of structural components inside the solidified Si-3.2B alloy/(h-BN-24ZrO₂-6SiC) sessile drop couple, non-destructive CT inspections were carried out before cutting the samples. Exemplary CT images of the couple are shown in Fig. 6, while a video showing the full 3D-CT scan is available as the Electronic Supplementary Material 3.

On contrary, the LM and SEM inspections of the cross-sectioned Si-3.2B alloy/h-BN composite couple after the thermocycling experiment between 1300 – 1450 °C

Fig. 6 The results of CT examinations of the Si-3.2B alloy/h-BN composite solidified couple after the step-heating experiment: a general view (a); the interface area showing a discontinuous layer composed of B_4C and SiC crystals (b); a distribution of borides and carbides in the vicinity of drop surface and at the drop/substrate interface (c–e)

revealed a much less extensive structural evolution (Fig. 7a). Although, the internal structure of the Si-3.2B alloy (Fig. 7b) seems to be only slightly different than that obtained in the material cooled down from 1750 °C, interface areas were visibly disparate. First of all, the presence of neither silicon borides distributed in the close vicinity of drop surface nor the (B₄C+SiC) product layer at the alloy/ceramic interface, was observed. In fact, only a few small SiC crystals were detected at the drop/substrate interface (Fig. 7c). This difference between examined samples can be justified by the following interconnected reasons:

1. *a strong effect of temperature on solubility* of boron in silicon. According to the Si-B binary phase diagram [18], the solubility limits at 1450 and 1750 °C are 5.9 and 14.16 wt% (14 and 30 at.%), respectively. Thus, it is reasonable to conclude that at temperature as high as 1750 °C, a much more boron (needed for the formation of interfacial borides) is dissolved in molten alloy from the contacting h-BN based ceramic.
2. *a limited interaction* between the molten Si-B alloy and the composite at temperatures below 1450 °C (i.e. a hindered dissolution of h-BN matrix and decomposition of primary SiC crystals).

Above mentioned findings are in line with the results of structural characterization of the cross-sectioned (h-BN+SiC+ZrO₂) substrates after the high-temperature tests (Fig. 8). A clearly visible Zone of Internal Reaction (ZIR) may be distinguished even in low-magnification images (Fig. 8a and d). What should be noted is that the ZIR is much deeper in the case of the sample tested at higher temperatures (up to 1450 °C). The same substrate appearance characterized by an existence of highly porous SiC-free outer part and reacted/unreacted transition area was observed in our previous work on the Si/h-BN composite system tested under the same conditions [16]. As

previously, the structural evolution of the examined h-BN-based composite upon the high temperature exposure was dominated by reactions taking place as follows:

1. *melting and evaporation* of native B₂O₃ boron oxide that is introduced during sintering of the h-BN composite. B₂O₃ melts at $T_m = 452$ °C [21] and under non-oxidizing conditions it quickly evaporates (under atmospheric pressure it starts at 1227 °C, while under vacuum the evaporation takes place at much lower temperatures) [22]. The existence of liquid boron oxide supports a decomposition of SiC particles through the following reaction [22]:

2. *reactions between the composite components* (h-BN and ZrO₂) facilitated by a thermal destabilization of primary SiC phase in contact with liquid boron oxide and/or Si-B melt. As it was theoretically and experimentally documented by Yan et al. [23], at temperature above ~ 1480 °C, h-BN reacts with zirconia and carbon (coming from a destabilization of SiC) to form zirconium diboride:

What should be noted is that both reactions (1 and 2) are assisted by gaseous products. As a consequence, the porosity is formed within the outer part of the composite substrate. However, a comparison of LM images (Fig. 8b and e) shows that the extent of the abovementioned structural evolution is much higher in the sample subjected to the step-heating up to 1750 °C than that after the thermocycling experiment between 1300 – 1450 °C. In the former case, a depth of SiC-free ZIR characterized by a coexistence of zirconium borides and porosity (Fig. 8c) was ~1700 μm (including also the intermediate

Fig. 7 The results of LM and SEM/EDS examinations of the cross-sectioned Si-3.2B alloy/h-BN composite couple after the thermocycling experiment (15 cycles of heating/cooling between 1300 – 1450 °C): a general view of the solidified Si-3.2B alloy (a); a microstructure of solidified drop showing a presence of Si+SiB₃ eutectic features (b); a few SiC particles formed at the Si-3.2B alloy/h-BN composite interface (c)

Fig. 8 The results of LM and SEM examinations of the cross-sectioned Si-3.2B/(h-BN-24ZrO₂-6SiC) couples after the high temperature wettability tests: step-heating at temperatures up to 1750 °C (a–c) and thermocycling between 1300 – 1450 °C (d–f). Please note various magnifications used in (b) and (e)

reacted/unreacted area). On the other hand, in the latter one only a degradation of the h-BN matrix (related to the formation of volatile boron oxide) was observed at depth of $\sim 480 \mu\text{m}$, while the morphology and chemistry of ceramic particles seem to be not strongly affected (Fig. 8f). All phases marked in Fig. 8c and f were identified based on the results of detailed SEM/EDS and XRD analyses (as in our previous work [16]). Therefore, it is concluded that in order to avoid extensive degradation of the examined h-BN composite, its operational temperature should not exceed 1450 °C (under conditions used in this study). However, regarding the predicted application in LHTES systems, this temperature limitation still allows using the h-BN-24ZrO₂-6SiC composite as the container material for Si and Si-3.2B based PCMs, as long as the operating temperature will not be substantially higher than their melting points (1414 and 1385 °C, respectively).

4 Conclusions

In this work, the high temperature interaction between the eutectic Si-B alloy and the commercially available h-BN composite was experimentally examined for the first time. Two types of sessile drop experiments were carried out: a step-heating up to 1750 °C, and a thermocycling composed of 15 cycles of melting/solidification of the Si-3.2B alloy. Based on the results of performed experiments and structural characterization supported by appropriate data from the literature, the following conclusions are drawn:

1. The Si-3.2B alloy exhibits a lack of wettability with the h-BN composite at temperatures up to 1750 °C. The Si-3.2B alloy shows a prominently lower wettability with the h-BN-24ZrO₂-6SiC composite, than the pure silicon examined under the same testing conditions [15].

2. The melting/solidification behavior of the Si-3.2B alloy is characterized by a good repeatability in consecutive thermal cycles and seems to be not affected by interaction with the h-BN composite.
3. The interaction between the Si-3.2B alloy and the h-BN-24ZrO₂-6SiC composite is dominated by a substrate dissolution/precipitation mechanism. The mechanism is much more active at higher temperatures, where a discontinuous interfacial product layer made of SiC and B₄C is produced.
4. The examined h-BN composite undergoes a structural evolution upon high-temperature experiments applied in this study. When temperature was not higher than 1450 °C (i.e. during the thermocycling experiment), a degradation of the composite was limited to melting and formation of volatile boron oxide. However, at higher testing temperatures (up to 1750 °C) reactions taking place between the composite components leads to a drastic change in the material structure assisted by the formation of porous near surface area. Nevertheless, it still makes it suitable for the predicted Si-B based LHTES system as long as abovementioned temperature restrictions will be kept.

5 Electronic Supplementary Materials

The following supplementary materials are available in the online version of this article:

1. *Electronic Supplementary Material 1* - the video clip recorded during the sessile drop test of Si-3.2B/(h-BN-24ZrO₂-6SiC) couple performed by the step heating procedure (up to 1750 °C);
2. *Electronic Supplementary Material 2* - the video clip recorded during the sessile drop test of Si-3.2B/(h-BN-24ZrO₂-6SiC) couple containing 15 cycles of heating/cooling between (up to 1300 – 1450 °C);
3. *Electronic Supplementary Material 3* - the video clip showing a full CT scan of the solidified Si-3.2B/(h-BN-24ZrO₂-6SiC) sessile drop couple subjected to the step heating experiment (up to 1750 °C).

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Compliance with Ethical Standards

Conflict of interests The authors declare that they have no conflict of interest.

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