Simultaneous Differential Thermal Analysis and Thermogravimetric Analysis of Si-30B Alloy

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This article focuses on the experimental determination of the transformation temperature of Si-30B alloy in the temperature range of 25–1820 °C in a flowing gas atmosphere (He, 99.9992%) carried out by simultaneous differential thermal analysis and thermogravimetric analysis (DTA–TG) using a graphite container. The DTA curve during heating showed the presence of two critical temperatures, i.e., $T = 1380.7$ °C and $T = 1532.0$ °C. The first one corresponds to the melting point of a eutectic system (Si + SiB₆). The high-temperature interaction and reactivity between the alloy and the container during DTA–TG test were evaluated by scanning electron microscopy coupled with energy-dispersive x-ray analysis. The results have demonstrated that the graphite container reacts with both liquid silicon and boron dissolved in liquid constituent of the alloy to form SiC and B₄C, respectively.

Keywords DTA, graphite container, reactivity, Si-B alloys, TG

1. Introduction

Recently, the Si-B alloys have been proposed as phase change materials (Ref 1) for ultra-high-temperature latent heat thermal energy storage (LHTES) because of high theoretical values of the latent heat of both silicon (1800 J/g) and boron (4650 J/g) (Ref 2). However, the ultra-high melting temperatures of Si and B (1414 and 2076 °C, respectively) and the presence of high-melting phases in Si-B alloys make experimental estimation of their critical temperatures by container-assisted methods such as differential thermal analysis (DTA) and thermogravimetric analysis (TG) very difficult. Due to the very high reactivity of molten Si with many commercial refractories, such as silica, alumina, magnesia (Ref 3), SiC, Si₃N₄, AlN (Ref 4) and graphite (Ref 5, 6), and currently not yet recognized interaction of pure Si with refractories at $T > 1500$ °C, the phase transformation analysis using DTA–TG appears to be very challenging. The key factor in these types of measurements is the choice of a suitable container material, which should be non-wettable and non-reactive in contact with liquid metal tested.

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According to the available literature, pure graphite is widely used for the fabrication and processing of metallurgical and photovoltaic grade silicon, this being mainly due to its low cost combined with a favorable set of thermophysical and utility properties (Ref 2–9), such as thermal expansion compatible with Si, good thermal shock resistance, excellent machinability, high-temperature stability and high thermal conductivity. Moreover, molten Si reacts with graphite to form a continuous interfacial layer of SiC that may play a role of barrier coating preventing further degradation of graphite. This phenomenon, known as passive-layer formation, was adopted in “self-crucible” concept for melting Si-B alloys and storage of Si-B melts in dense graphite crucibles (Ref 2). It should be highlighted that for such ultra-high-temperature DTA–TG measurements, the replacement of graphite containers with containers made of other materials is also problematic because in many experimental devices it may affect the harmonization of surrounding parts and, consequently, result in the need to use alternative new materials. Among others, good physicochemical compatibility between the container material and its holder is also required. For example, in the Netzsch STA 449 F3 Jupiter[®] device used in this study, the W–Re holder is suitable for graphite containers but it is not recommended for h-BN containers that show negligible reactivity with Si-B alloys up to 1760 °C (Ref 1, 10).

In fact, no standard laboratory test methods are currently available for examination of the properties of semiliquid or liquid silicon-based alloys at ultra-high temperatures. In this study, taking into account the very limited reported information on experimental procedures and setups, graphite refractory was the first choice because it is a common container material used in commercially available devices for measurement of the thermophysical properties of materials (Ref 8). Graphite is also used as a crucible material for the manufacture of this group of alloys (Ref 2).

In this study, phase transformations taking place in the selected Si-B alloy were examined in a wide range of temperatures (25–1820 °C) in flowing He atmosphere using the combined DTA–TG method of thermal analysis. The simultaneous DTA–TG technique was applied for the experi-

Fig. 1 SEM microstructure of as-cast Si-30B alloy with the results of chemical analysis at marked points collected in Table 1

Table 1 Chemical composition of Si-30B alloy in market points (Fig. 1)

Point	Element, at. %			Phase
	B	C	Si	
1	82.0	16.1	1.9	B ₄ C
2	82.2	15.7	2.1	
3	66.9	8.1	25.0	SiB ₃
4	...	...	100.0	Si

mental estimation of critical temperatures of the selected Si-B alloy.

2. Experimental

The following materials were used in this study:

1. Si-B alloy with a nominal chemical composition of Si-30B (wt.%) corresponding to hypereutectic alloy (Ref 11) was produced from batch materials (Si: 99.99%; B: 99.9%) by the induction melting in a graphite crucible. The alloy was produced by the Department of Materials Science and Engineering, Norwegian University of Science and Technology.
2. A commercial DTA–TG conical graphite container of 0.15-ml capacity (GB427607 type, Netzsch Company (Ref 12)) was produced by machining from a graphite block with open porosity > 15%, wall thickness ~ 0.3 mm and upper diameter ~ 5.60 mm.

The DTA–TG measurements were carried out using a commercial thermal microbalance Netzsch STA 449 F3 Jupiter® device equipped with a tungsten furnace and W–Re DTA–TG sample holder. Mass gains and temperatures were measured in the temperature range of 25–1820 °C in a flowing gas atmosphere (He, 99.9992%, 100 ml/min) at a heating/cooling rate of 20 °C/min. Before the DTA–TG experiment, a small sample of alloy (40.766 mg) was cleaned with acetone and air-dried.

The thermometry of the sensors was checked with three pure standards (Ni-C, Pd-C, W-C) using commercial conical graphite containers (Netzsch); other conditions were the same as applied in the investigation of Si-B alloy (flowing He; heating/cooling rate). The temperature accuracy of the Me-C

Fig. 2 Materials before the DTA–TG test: (a) SEM image of alloy sample; (b) photograph of conical graphite DTA–TG container

Fig. 3 TGA–DTA curves of the alloy sample during continuous heating up to 1820 °C

Fig. 4 TGA–DTA curves of the alloy sample during continuous cooling down to 400 °C

standards/substances was about ± 1 K. This value included the uncertainty itself and the repeatability when several samples of the same type were measured. For the calculation of critical temperatures, Proteus[®] Analysis 6.1 software was used. Structural characterization was performed by the scanning electron microscopy (SEM) using a TM3000 Hitachi device equipped with energy-dispersive x-ray spectroscopy (EDS) analyzer.

3. Results and Discussion

Prior to the DTA–TG measurements, the as-received Si-30B alloy was subjected to microscopic examinations with SEM + EDS to evaluate the alloy chemical composition in as-cast state (Fig. 1 and Table 1).

Analysis of the data compiled in Table 1 shows that the alloy contains carbon in an amount that, depending on the place of analysis, is in the range of 8.1-16.1at.%. The presence of

Fig. 5 Si-B phase diagram—literature experimental data (Ref 11)

Fig. 6 Photographs of materials after the DTA-TG test: fragments of graphite container (a-c), residual alloy sample (b)

carbon is caused by the method of alloy manufacture, i.e., the fusion of Si and B in a graphite crucible. Due to the limitation of the EDS method, the results obtained show only the tendency to changes in the carbon content.

The representative results of the SEM + EDS analysis of alloy sample before the DTA-TG test showed its complex and inhomogeneous structure (Fig. 1a). In the silicon matrix, there are two types of precipitates of dissimilar morphology, i.e., regular crystals and needles. From the EDS analysis of the chemical composition (Fig. 1a, Table 1), it can be assumed that needles (point 1) and dark gray regular crystals (point 2) are composed of the B_4C phase, while the chemical composition of light gray regular crystals (point 3) suggests the SiB_3 phase.

After the SEM + EDS examinations, the alloy sample was (Fig. 2a) placed in a conical graphite container (Fig. 2b).

After placing the sample container and reference container in a thermal microbalance chamber, the test system was rinsed

with He for 10 min at 25 °C and then the DTA-TG test was started. The runs of the DTA-TG curves plotted in the temperature range including melting and solidification of alloy sample are presented in Fig. 3 and 4, respectively.

During heating of the alloy sample up to 1800 °C, its mass is constantly changing (Fig. 3). The total change in alloy mass is $\Delta m_2 = -0.43$ mg for $T > 1400$ °C, and the alloy mass decreases because the sample starts to evaporate.

Three peaks are visible on the DTA curve: (1) endothermic peak at $T_{\max} = 1380.7$ °C and (2) exothermic peaks at $T_{\max} = 1389.2$ and 1532.0 °C, respectively. In accordance with the Si-B phase diagram (Fig. 5) (Ref 11), the peak recorded at 1380.7 °C corresponds to the melting point of a eutectic (Si + SiB_6). Despite the fact that the recorded melting temperature of binary eutectic is by 4.3 °C lower than the temperature given in the literature (Ref 11), according to the same authors it may be 1385 ± 15 °C. Additionally, this difference may be due to the presence of carbon in the examined alloy.

The shape and course of the exothermic peaks can indicate that: (1) a reaction has taken place between the container material and the alloy sample; (2) a phase transformation can occur; and (3) the W-Re sensor material reacts with the alloy, which makes proper interpretation of the DTA results difficult.

During cooling of the alloy down to 400 °C, no change in mass was observed, while on the DTA curve, only one peak was visible at $T_{\max} = 1335.7$ °C, which corresponded to the liquid-solid transformation.

After the DTA-TG test, an attempt was made to remove the graphite container from its holder. However, it could not be separated from the holder, while the next attempt to pull it out resulted in damage of the container (Fig. 6). During removal of the broken parts of graphite container (Fig. 6a), silver-black fragments (Fig. 6c) were noticed; their shape resembled the shape of the graphite container. During extraction of the silver-black fragments, they were broken.

Visual examinations of the alloy sample showed its irregular shape and sponge-like structure, indicating that it represents the residual amount of the alloy that was not completely melted during high-temperature test (Fig. 6b and 7a-d).

The SEM + EDS analysis of the solidified alloy sample has revealed its shape resembling a “cauliflower” with two-color structure (Fig. 7a-d). The chemical composition of the dark gray area corresponded to 72.7 at.% B, 15.8 at.% C and 11.5 at.% Si (SiB_3 , B_4C phases). The chemical composition of the light gray area corresponded to 52.7 at.% B, 12.1 at.% C and 35.2 at.% Si (SiB_3 , B_4C phases).

The structural characterization (SEM + EDS) of the fragment of graphite container was made on its both inner and outer surfaces (Fig. 8, 9). On the inner surface, two areas of a different color and morphology were detected (Fig. 8). The light gray area (Fig. 8c) was composed of regular precipitates whose chemical composition is given in Table 2. The dark gray area was covered with a “grid” of light color precipitates corresponding to the area of liquid metal infiltration (Fig. 8d). The chemical compositions and phases are given in Table 2.

The presence of the SiC and B_4C phases shown in Table 2 can be explained based on the Si-B (Ref 11) phase systems, Si-

Fig. 7 Detailed analysis of alloy sample after the DTA–TG test: (a) photograph of residual alloy sample; (b) its SEM image; (c) SEM image of magnified area marked in (b); (d) SEM image of magnified area marked in (c) with EDS analysis made at points 1 and 2

B–C liquidus projection phase diagram (Ref 2) and Si–B–C phase diagram (Ref 2). During heating of the alloy sample at a temperature of about 1380 °C, a eutectic (Si + SiB₆) appeared in the graphite container. According to the Si–B phase diagram (Ref 11), it might contain about 3.2 wt.% B. At the graphite container/silicon interface, the formation of silicon carbide crystals began immediately after the silicon melting (Ref 13) according to reaction (1):

With the temperature increase to 1800 °C, the time of interaction of the liquid phase with the container material increased and finally amounted to 50 min. According to the Si–B–C liquidus projection phase diagram (Ref 2), at the alloy/graphite container interface, a liquid with 3.2 wt.% boron content coexists with the SiC phase. In the system, reaction (2) between boron from the solution and SiC, described by the authors of (Ref 2), took place:

Examinations of the outer surface of the fragment of graphite container showed a large number of light gray precipitates in the shape of platelets (Fig. 9a) with an average size of 20–30 μm (Fig. 9b). The chemical composition (Table 3) of the plate-shaped precipitates (points 1–2) showed the presence of SiC and W. The presence of W was caused by the reaction between Si and the holder material (W–Re).

The presence of SiC in the form of plate-shaped precipitates is probably associated with the porosity of the container material (open porosity > 15%) combined with the small thickness of the container walls (~ 0.3 mm).

The analysis of the results obtained in this study during experiments performed up to a temperature of 1800 °C shows key methodological problems of testing molten Si–B alloys by container-assisted methods, such as DTA–TG. Due to the high melting temperature of high-boron Si–B alloys coupled with their high reactivity in contact with graphite, the self-crucible concept successfully applied in the fabrication and processing practice of metallurgical and photovoltaic grades of silicon at a temperature ≤ 1450 °C is not suitable for the ultra-high-

Fig. 8 (a) SEM image of the fragment of graphite container with marked two areas (light and dark); (b) SEM image of the dark gray area; (c) SEM image of the light gray area with EDS analysis made at points 1 and 2; (d) SEM image of the dark gray area with EDS analysis made at points 3-7

Fig. 9 (a, b) SEM images of the light gray precipitates; (b) with the results of EDS analysis made at points 1-3 and collected in Table 3

temperature measurements of Si-B alloys. The main reason of dissimilar findings is related to a strong degradation of commercially available graphite containers since, contrary to large-scale industrial crucibles, their thickness (about 0.5 mm)

is comparable with the depth of liquid metal infiltration. (Even at a much lower temperature of about 1450 °C, it varies from 0.25 to 0.40 mm, depending on the graphite type, its porosity and size of pores (Ref 3-9).)

Table 2 The results of local analysis of chemical composition by EDS analysis (at.%) of the inner graphite container surface

Point	Element, at.%			Phase
	B	C	Si	
1	19.7	50.7	29.5	SiC
2	25.0	43.2	31.8	SiC
3	77.4	19.4	3.2	B ₄ C
4	77.6	18.4	4.0	B ₄ C
5	79.3	18.0	2.7	B ₄ C
6	77.8	19.1	3.2	B ₄ C
7	67.1	14.00	18.9	SiB ₃

Table 3 Results of the local analysis of chemical composition by EDS analysis (at.%) of points precipitates marked in Fig. 9(b)

Point	Element, at.%			Phases
	W	C	Si	
1	25.9	56.3	17.7	SiC, W
2	19.2	27.3	53.4	SiC, W
3	33.0	67.0	...	SiC, W

4. Summary

The DTA curve during heating of Si-30B alloy showed the presence of two critical temperatures, i.e., $T = 1380.7^\circ\text{C}$, which corresponds to the melting point of the eutectic (Si + SiB₆), and $T = 1532.0^\circ\text{C}$, which corresponds to the eutectic reaction with sensor material. Determining the melting and solidification temperatures of Si-B alloys by means of DTA–TGA using graphite crucibles is difficult and creates major methodological problems. Our results showed that to minimize the risk of destruction, graphite containers with larger thickness, smaller pore size and higher density should be used either with or without a protective coating such as BN, which has been successfully used in DSC measurements with liquid Si (Ref 13).

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