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Measurements of temperature and heat of phase transformation of pure silicon by using differential scanning calorimetry

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Abstract

Differential scanning calorimetry (DSC) technique has been applied for the experimental determination of temperature and heat of phase transition of pure silicon (7 N) during heating and cooling cycles at the rate of 10 K min^{-1}. The measurements were carried out in the temperature range of 25–1450 °C in a flow gas atmosphere (Ar, 99.9992%) using three types of crucibles made of alumina, h-BN and alumina covered with h-BN coating. The following characteristics were estimated from DSC curves: melting point of silicon—1414 °C, the heat of fusion—1826 J g^{-1} and the heat of solidification—1654 J g^{-1}. It was found that the silicon evaporation phenomenon accompanying the tests had no effect on the measurements of temperature during solid-to-liquid and liquid-to-solid transformations and on the measurement of the latent heat of fusion. The effect of crucible type on the DSC measurements is discussed.

Keywords Silicon · Boron nitride · Alumina · h-BN coating · DSC · Latent heat of fusion · Latent heat of crystallization

Introduction

The continuous increase in thermal energy consumption in the world causes intensification of research on its acquisition and storage owing to the use of thermal energy storage (TES) systems [1]. Among different possible solutions for TES systems, those based on latent heat storage of phase change materials (PCMs) are the most efficient since they provide much higher storage density with a smaller temperature difference between storing and releasing heat [2].

Recently, Si and Si–B alloys have been recognized as promising high-temperature PCM candidates taking into account their theoretically high latent heat of fusion values (e.g., 1800 J g^{-1} and 4650 J g^{-1} for Si and B, respectively) [3]. Therefore, reliable information on the latent heat of fusion Si–B alloys is of a great practical importance. In the open literature, there are no data for Si–B or Si–B-based alloys while only a few data are available for pure Si and B. For pure Si, experimental values of melting temperature and latent heat of fusion are reported in [4–13] and they are scattered and even contradicted. Their analysis suggests that the values the latent heat of fusion (1851 J g^{-1}) and melting temperature (1414 °C) reported by Yamaguchi et al. [4] are the most reliable. They were experimentally determined by a drop calorimetry method using a sealed hexagonal boron nitride (h-BN) container in the temperature range of 427–1547 °C. However, in the study [4], the value of the latent heat of solidification of pure Si was not specified. For pure boron, situation is more complicated because only theoretical values of thermophysical properties are reported in the literature.

This work was performed in a frame of AMADEUS project [3], and it discusses the results of differential scanning calorimetry measurements (DSC) of the critical temperatures of pure Si and latent heat of fusion/latent heat of crystallization in the temperature range from 25 to 1450 °C under flowing Ar using a commercial thermal microbalance Netzsch STA 449 F3 Jupiter® and commercial crucibles made from boron nitride and alumina.

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Experimental

The following materials were used in this work:

(1) Ultrahigh purity silicon (7 N)—the selected silicon material was amorphous polysilicon produced by the commercial Siemens process, in which Si is precipitated from high-purity silane (SiH_4) or trichlorosilane ($HSiCl_3$) gases at elevated temperatures;
(2) Commercially available hexagonal boron nitride (h-BN);
(3) Alumina (Al_2O_3) Netzsch crucibles;
(4) Commercially available h-BN spray Henze HeBoCoat® 401E (ceramic slurry) for alumina.

DSC measurements were carried out using a commercial thermal microbalance Netzsch STA 449 F3 Jupiter® device equipped with Pt–Rh DSC-C_p sample holder. Estimation of critical temperatures and latent heat of fusion/latent heat of crystallization was done with a Netzsch Proteus Thermal Analysis 6.1.0 software. DSC tests were performed in the temperature range from 25 to 1450 °C under flowing argon with a heating/cooling rate of 10 K min^{-1}. The tests were carried out in protective atmosphere (Ar) in order to suppress Si vaporization because in vacuum, Si already evaporates at a temperature of 1337 °C [14], i.e., below melting point of Si.

For the selected temperature range, sensitivity and temperature calibrations were made with five pure metals (In, Bi, Al, Au, Ni) using commercial Al_2O_3 crucibles (Netzsch) and the same other conditions as those applied for investigation of pure Si (flowing Ar; heating/cooling rate of 10 K min^{-1}).

After the DSC tests, the crucibles were removed from the DSC holder and then subjected to structural evaluations by using scanning electron microscope (Hitachi 3000) and nondestructive analysis by 3D-computed tomography imaging (Nanotom 180). CT examinations were performed with the following exposure parameters: voltage—90 kV, current—170 μA and voxel size—4.0 μm vox^{-1}. Computer processing and data analysis were carried out in a specialized datos/x-reconstruction using VGStudio Max 2.0 software.

Results and discussion

DSC test with h-BN crucible (Test #1)

The first DSC test was performed with h-BN crucibles, i.e., both sample crucible and reference crucible were made from h-BN. The selection of h-BN crucibles was based on the findings of the detailed study on the interaction between molten Si and h-BN recently reported by Polkowski et al. [15] who evidenced negligible reactivity of the Si/h-BN system in the temperature range of our interest. Commercial h-BN crucibles of NGB808836 type (85 μl) [16] produced by Netzch were used in this study.

The silicon sample was cut into small piece (30.43 mg), cleaned with acetone and placed in the middle of the h-BN sample crucible. After placing the sample crucible and reference crucible in a thermal microbalance chamber, the test system was rinsed with argon of 99.9992% purity for 30 min at 25 °C and then the DSC test was started. It should be highlighted that the Proteus Analysis 6.1 software used in this study does not take into consideration the selection of h-BN crucibles. Therefore, according to the recommendations by the producer of DSC device, the calibration was made for Al_2O_3 crucibles.

The runs of DSC curves plotted upon heating and cooling of Si sample in h-BN crucible are presented in Fig. 1a and b, respectively. There is one endothermic effect on the DSC curve recorded during Si melting (Fig. 1a). After reaching the temperature of 1418 °C, the Si sample starts melting while the maximum peak is at 1434 °C. The calculated latent heat of fusion is 1114 J g^{-1}. During cooling, one exothermic peak is visible (Fig. 1b). The solidification of liquid Si starts at 1399 °C and exothermic peak reaches its maximum at 1387 °C while the calculated latent heat of solidification is 1002 J g^{-1}.

To perform visual examinations of the solidified Si sample, an attempt was made to open the crucible. Unfortunately, it failed and the lid could not be removed. Therefore, in the next step, nondestructive analysis by 3D-computed tomography (CT) imaging [17] was used to see the crucible interior. Figure 2a depicts the representative 3D-CT image of the h-BN crucible with solidified Si sample inside, while 2D-CT image of cross section of the crucible wall is shown in Fig. 2b. The CT analysis evidenced that the solidified Si sample did not contact the lid, and its one side was on the crucible bottom though another side was connected with the crucible wall (Fig. 2a). The crucible wall was porous (Fig. 2b), and occasionally it contained some light precipitates.

The more detailed CT analysis of the crucible lid showed its connection with one crucible wall (Fig. 3a), and the presence of some light precipitates inside connection and lid hole (Fig. 3b).

Moreover, numerous pores in the crucible wall were detected that might be responsible for weak mechanical resistance of h-BN crucible and its failure in the next attempt to separate the lid from the crucible. In this attempt, the crucible fell into pieces under the effect of a small mechanical force. The Si sample extracted from the crushed crucible was weighed on an analytical balance, and a mass loss of $\Delta m = 5.8\%$ was recorded. Most probably,

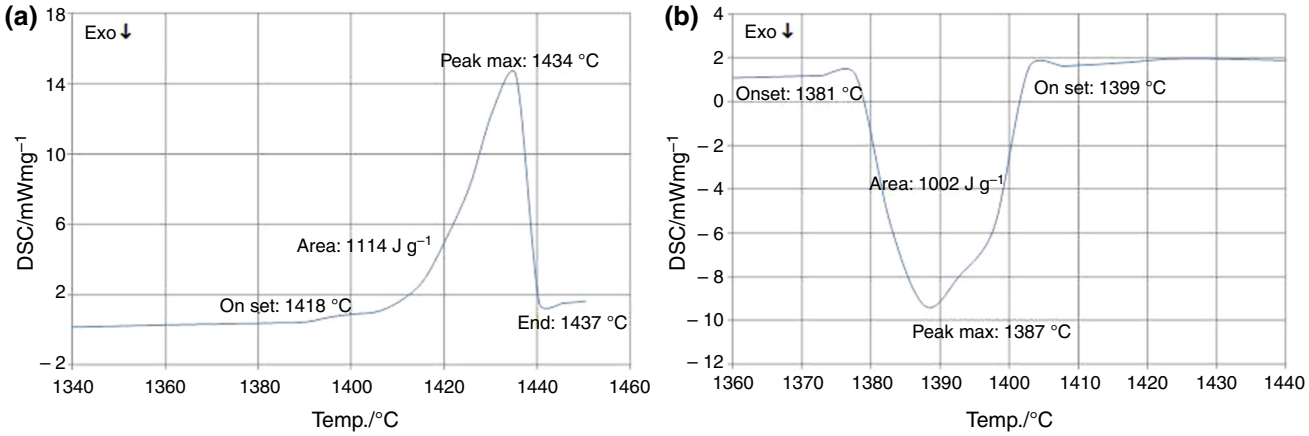

Fig. 1 The DSC curves recorded during continuous heating up to $T = 1450$ °C (**a**) and subsequent cooling up to $T = 1360$ °C (**b**) in h-BN crucible (Test #1)

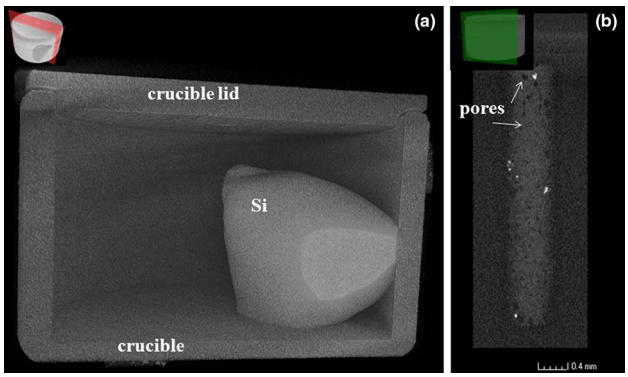

Fig. 2 Representative CT images after DSC test: **a** Si sample inside h-BN crucible, **b** part of h-BN crucible wall with visible pores and precipitates (inserts in the top of images correspond to *XZ* plane)

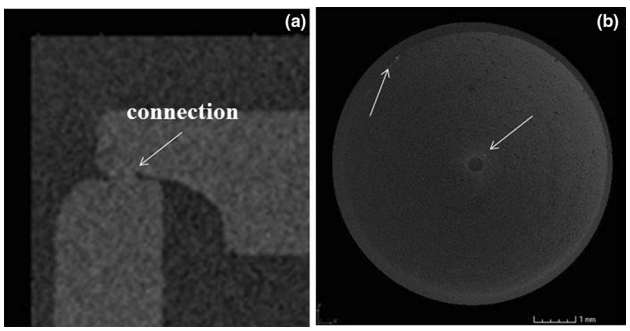

Fig. 3 The CT images of crucible lid: **a** connection between h-BN crucible and lid, **b** lid with light precipitates

this mass loss was caused from an evaporation of Si followed by its partial condensation at the crucible walls. This finding was documented by the presence of bright particles on the crucible walls and lid. Additionally, some parts of evaporated Si were removed from the crucible through the hole in the lid. In the next step, one single fragment of the crucible was subjected to detailed SEM examinations (Fig. 4) that also confirmed the CT observations, i.e., the porosity is formed in the crucible walls during DSC test.

Degradation of the h-BN crucible may follow the same route as the thermal decomposition of h-BN composite ($BN + B_2O_3$) described by Eichler and Lesniak [18] who described thermogravimetric measurements performed in a Netzsch STA 429 thermobalance under different atmospheres (Ar, vacuum, air and nitrogen) in the temperature range from 25 to 1600 °C. They discovered that in both vacuum and air atmosphere at a temperature of about 1100 °C, the mass of h-BN changes and it grows in the air and decreases in a vacuum. The mass increase in the air atmosphere is most probably associated with the oxidation of h-BN and the formation of boron oxide, whereas the decrease in mass in a vacuum is most probably related with the decomposition of h-BN. Hildenbrand and Hall [19] described decomposition process of h-BN recorded by effusion method at temperature range of 1577–1887 °C. This process according to the reaction (1), where N_2 is the only significant gaseous species in the temperature range, is investigated as:

$$BN(s) = B(s) + N_2(g) \quad (1)$$

J. Eichler and Ch. Lesniak [17] observed that thee mass decrease under the Ar atmosphere starts at a temperature of about 1420 °C, while in nitrogen, it takes place at a temperature of about 1500 °C.

Thus whatever the reason is (oxidation or decomposition of h-BN, Si evaporation), a change in the mass of the crucible and Si sample during DSC tests increases the error in the measurements of both latent heat of fusion and latent heat of crystallization.

DSC test in alumina crucible coated with h-BN spray (Test #2)

Taking into account the possible decomposition of the h-BN crucibles during DSC measurements, the next DSC test was performed in the Al_2O_3 crucibles that show high stability in the temperature range of our interest. However, in view of the recommendations by the producer [16], the Al_2O_3 crucibles should not be used at high temperatures for testing Si due to possible chemical reactions of liquid Si with Al_2O_3. In order to limit the reactivity between liquid Si and the Al_2O_3 crucible, its surface was covered with h-BN coating by using a commercial Henze HeBoCoat® 401E spray. The choice of this coating was based on the findings from own study [15] dedicated to the investigation of the effect of Henze HeBoCoat® 401E spray deposited on the SiC substrate on suppression of its reactivity with liquid Si at temperatures close to the melting point of Si.

The procedure for coating the Al_2O_3 crucibles (sample crucible + reference crucible) with the h-BN coating involved three stages: (1) ultrasonic cleaning of crucibles with acetone for 5 min at 25 °C and then drying in a stream of warm air; (2) sputtering on internal surfaces of crucibles, h-BN spray; (3) heating crucibles in a thermal microbalance Netzsch STA 449 F3 Jupiter® device for 30 min under an Ar atmosphere at 800 °C. The sensitivity and temperature calibrations were made with five pure metals (In, Zn, Bi, Al, Au and Ni) using h-$BN^{coating}/Al_2O_3$ crucibles and the same other conditions as those applied for investigation of pure Si (flowing Ar; heating/cooling rate of 10 K min^{-1}).

For the first DSC test (Test #2.1), only internal surfaces of crucibles were covered by h-BN coating. The crucible lids were uncoated. The weighed (39.49 mg) and degreased sample of Si was placed in a sample crucible. During DSC measurement in cooling segment, the abnormal run of DSC curve was observed and measurement was stopped. The run of heating DSC curve is shown in Fig. 5. During heating, one endothermic peak was recorded. After reaching temperature of 1402 °C, the Si sample melts (corresponding latent heat of fusion measured was 409.5 J g^{-1}) and peak reaches a maximum at 1434 °C.

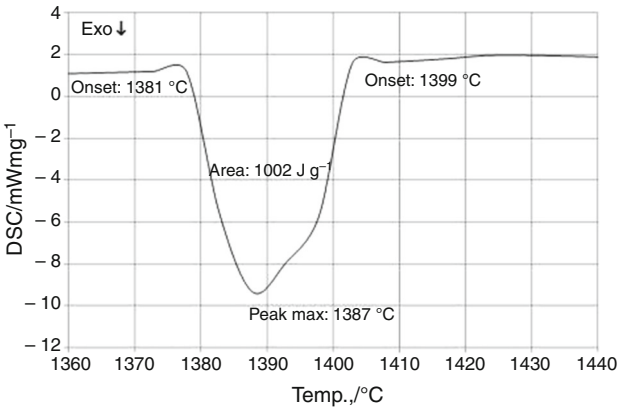

Fig. 5 The DSC curve recorded during continuous heating up to T = 1450 °C in h-$BN^{coating}/Al_2O_3$ crucible (Test #2.1)

At the end of the test, the crucible with the sample was opened and it was found that the Si sample changed its position and it was connected with the lid of the crucible (Fig. 6a). Visual observations showed that the solidified Si sample had the shape of a drop from which a cone protruded. The presence of the cone was associated with a change in the volume of the Si sample during solidification as it was also observed in [19]. Therefore, it can be assumed that the phenomenon of the cone formation during solidification caused the change in the Si sample position due to: (1) too large mass of the sample because the growing cone was so high thus it touched the uncoated Al_2O_3 lid; (2) easy transfer of the Si drop to the surface of the lid due to liquid Si wets well alumina [20]. To determine the mass of the Si sample after the test, an attempt was made to detach the drop from the lid. However, the drop could not be separated; therefore, nondestructive analysis by computed tomography using 3D-imaging of the

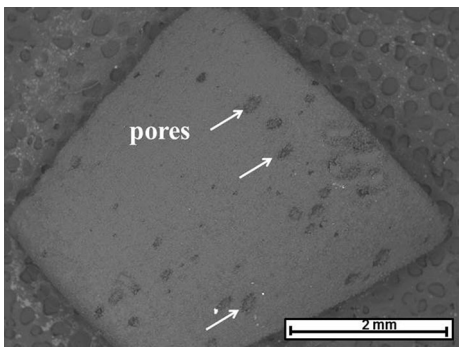

Fig. 4 SEM image of h-BN crucible wall fragment (top view)

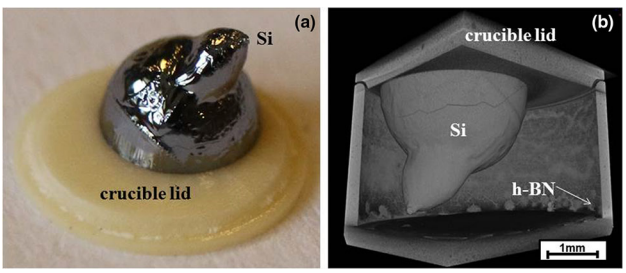

Fig. 6 Views of Si sample after DSC test: **a** photograph of solidified Si sample connected with alumina lid (upside down position of the lid), **b** 3D-CT image of alumina crucible coated with h-BN spray and covered with uncoated alumina lid showing Si drop solidified on the lid

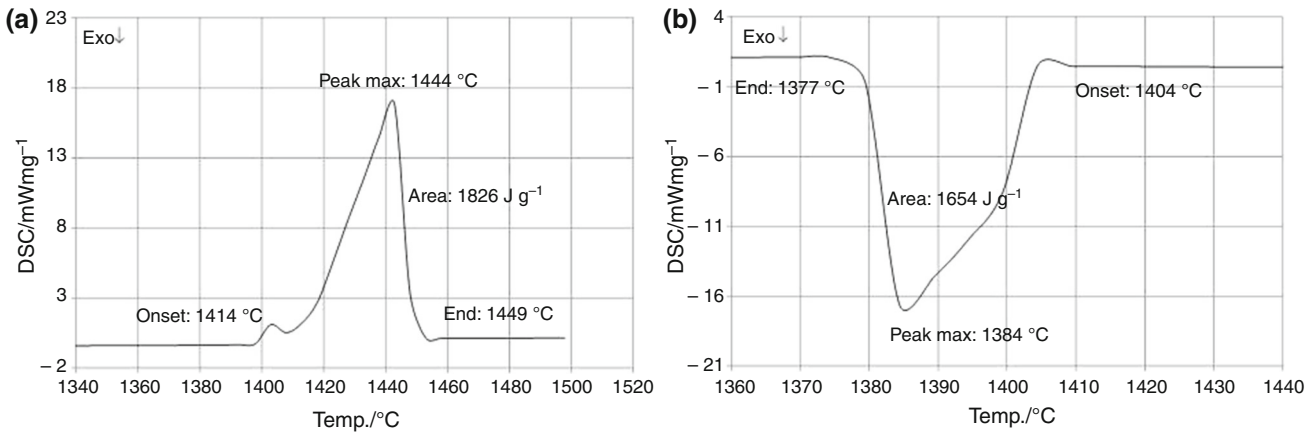

Fig. 7 The DSC curves recorded during heating up to T = 1450 °C (**a**) and cooling up to T = 1360 °C in h-BN^{coating}/Al_2O_3 crucible (**b**) (Test #2.2)

Table 1 The most important quantitative parameters extracted from the DSC heating and cooling curves

Heating/°C			Cooling/°C		
T_{onset}	T_{max}	T_{end}	T_{onset}	T_{max}	T_{end}
Test #1with h-BN crucible					
1418	1434	1373	1399	1386	1381
Test #2.1 with h-BN^{coating}/Al_2O_3 crucible					
1402	1434	1438	–	–	–
Test #2.2 with h-BN^{coating}/Al_2O_3 crucible					
1414	1444	1449	1404	1384	1377

Table 2 The values of the melting point, latent heat of fusion and solidification compared with the literature data [4–13]

Method	Crucible	Melting point/ °C	Latent heat of fusion/ J g^{-1}	Latent heat of solidification/ J g^{-1}	Refs.
Drop calorimetry	h-BN sealed capsule	1414	1720	–	[4]
n/a	n/a	1414	–	–	
n/a	n/a	1412	–	–	
n/a	n/a	1414	1790	–	[5, 6]
n/a	n/a	1414	1790	–	[7]
n/a	n/a	1410	1650	–	[8]
n/a	n/a	1414	1790	–	[9]
n/a	n/a	1412	1790	–	[10]
n/a	n/a	1410	1800	–	[11]
n/a	n/a	–	1790	–	[12]
n/a	n/a	1423	1800	–	[13]
DSC	Commercial h-BN crucible	1409[a]	1114[c]	1002[c]	This work
DSC	Commercial alumina crucible[b,d]	1409[a]	1826	1654	

[a]Melting point calculated as the average peak onset recorded during heating and cooling

[b]Crucible covered with h-BN coating

[c]The values underestimated due to different values of thermal conductivity of crucible

[d]Test #2

whole crucible was performed (Fig. 6b) in order to determine the volume of Si sample after DSC test. The volume of Si was amounted to 15.9 mm^3 that corresponds to the mass of 37.04 mg calculated taking into account the density of Si (2.32983 g cm^{-3}). Thus, in this DSC test, the mass change of Si sample (2.45 mg) Δm was 6.2%.

In order to avoid possible transfer of the molten Si sample to the lid, for the next DSC test (Test #2.2), both the alumina crucible and the alumina lid were covered with an h-BN spray while the mass of the Si sample was decreased up to 30.43 mg. The run of DSC curves in the temperature range including melting and solidification of Si is shown in Fig. 7. On the DSC curve plotted during Si heating, one endothermic effect is observed (Fig. 7a). After reaching the temperature of 1414 °C, the Si sample melts with corresponding heat of fusion = 1826 J g^{-1} and its maximum peak at 1434 °C. During cooling, one exothermic peak is visible on the DSC curve (Fig. 7b). The Si sample starts solidification at 1404 °C and its maximum peak at 1384 °C. The end of solidification is at 1377 °C with corresponding latent heat of solidification = 1654 J g^{-1}.

Contrary to the previous measurement, after Test #2.2 there was no any joint between the crucible and its lid. The crucible was opened, and the solidified Si sample was easily taken off the crucible due to a lack of bonding between them. The Si sample was then weighed on an analytical balance, and a mass loss of $\Delta m = 5.2\%$ was found. The most important quantitative parameters of the DSC curves are shown in Figs. 1a, b, 5 and 7a, b, and calculated temperatures are listed in Table 1.

The values collected in Table 1 show that the melting point of pure Si determined in the h-$BN^{coating}$/Al_2O_3 crucible is 1414 °C (Test #2.2) and 1402 °C (Test #2.1), whereas in the h-BN crucible, the melting point of Si is 1418 °C (Test #1). Differences in detected temperatures probably are due to dissimilar thermal conductivity of alumina and h-BN at the test temperature, i.e., alumina > 10 W m^{-1} K^{-1} (own studies); h-BN (25 W m^{-1} K^{-1}) [21]. In the case of measurements carried out in the h-BN crucibles, such a calibration (using Al_2O_3 crucibles) could additionally underestimate the heat values measured. In the case of Test #2.1, due to the change position of the sample the values for cooling process cannot be determined. The values of the melting point, latent heat of fusion and latent heat of solidification are collected in Table 2 and compared with previous studies using different methods [4–13].

Based on the literature data collected in Table 2, one may conclude that the melting point of pure Si is in the range of 1410–1423 °C [4–13] whereas the value of latent heat of fusion is between 1650 and 1800 J g^{-1}. The values of melting point obtained experimentally in this work, both in the h-BN crucible (1409 °C) and in the Al_2O_3 crucible (1409 °C), are consistent with the available literature. However, the latent heat of fusion recorded in this study differs by 712 J g^{-1} and in the case of the h-BN crucible, it is significantly lower than the values given in the literature.

Although in the reviewed literature (Table 2) there is no data on latent heat of solidification, the compatibility of the remaining experimental results (melting point and latent heat of fusion) recorded in the h-$BN^{coating}$/Al_2O_3 crucible allows accepting the latent heat value of solidification obtained for this crucible as a reliable and reference value. The difference of 172 J g^{-1} between the latent heat of fusion and latent heat of crystallization values recorded in the same DSC test may be due to the change in sample mass.

In the case of using the h-BN crucible, the values of both latent heat of fusion and latent heat of solidification are significantly lower than those obtained in the h-$BN^{coating}$/Al_2O_3 crucible, and despite a good agreement of the melting point value with the literature data, these values should not be considered reliable and used as a reference.

Conclusions

Based on the tests performed, it can be concluded that the differential scanning calorimetry with flow measurement enables experimental determination of the melting and solidification temperature of pure silicon coupled with measurement of the heat absorbed or released in the melting and solidification process. Due to compliance with the literature data, the obtained experimental values of melting temperature and the latent heat of fusion may serve as reference data. Despite the lack of the literature data on the value of the latent heat of solidification but taking into account a good agreement between the values of thermophysical properties measured in this study and those given the literature, we suggest that the heat of solidification obtained in this research can be used as a reference value.

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