The Use of Si-B Alloys in Thermal Energy Storage System

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Abstract. Si-B alloys are considered as phase change materials (PCMs) in the thermal energy storage (TES) systems due to their high latent heats and moderate temperatures. In order to successful apply them, proper Si-B alloy composition and a suitable ceramic refractory material that can survive long time corrosion at high temperatures should be determined. Here, we investigate serials of Si-B alloys with the B range of 2-11 mass % in graphite crucibles in the temperature range 1450-1750 °C. This work shows that the interaction between Si-B alloys and graphite goes into two stages. Single SiC is formed at the interface at the B content of 2 mass %. SiC and B4C are produced at the interface at the B contents of higher than 5 mass %. Additionally, the results of structural characterization are supported by thermodynamic calculation. These results provide reliable data in the use of Si-B alloys as PCMs in the TES systems.

1. Introduction

The mismatch between energy supply and electricity demand is a major problem in the use of renewable energy areas, e.g., wind energy and solar energy. Latent heat thermal energy storage (LHTES) is regarded as an effective way to solve this problem, where heat is stored in the form of latent heat. In this process, the materials play an important role in determining the overall performance of the storage system, which is referred to as phase change materials (PCMs) [1]. Most PCMs operate between solid-liquid transformations to store a large amount of energy in a small volume, providing some of the lowest storage material costs per unit energy [2]. Recently, Datas et al. [3] proposed the introduction of Si as a PCM due to its high melting point (1414 °C), high latent heat (1800J/g), high thermal conductivity (25 Wm⁻¹K⁻¹), low cost, and abundance on earth. However, the experiments of using pure Si in solar thermal energy storage [4] revealed some challenges. The most relevant engineering concerned was the damage to the container upon solidification, which was caused by the high volume expansion of Si [5]. Datas et al. [3] found that the most reasonable solution was to use Si-based alloys instead of Si to reduce the volume expansion of silicon, tune the melting temperature, and to increase the fusion heat.

The use of Si-B alloys as new PCMs is attractive due to the addition of B, of which the fusion enthalpy is 4650 J/g. Moreover, the volume expansion of Si-B alloys decreases with the addition of B [6]. It is proposed that Si-B alloy is a desired PCMs in the TES systems. There are, however, some scientific and technical challenges that need to be overcome before transferring it to real industrial applications. One question is the determination of the B content in the Si-B alloys, the phase formations in the Si-B alloys were hence investigated at the B content of 2-11 mass %. In addition, the
PCM containers used in the storage energy system should be experimentally evaluated to confirm its long durability and high reliability in the long-term energy storage period. Graphite is vastly employed for the production of crucibles due to its ease of machining, high-temperature stability and moderate ease of purification. Therefore, dense graphite is chosen to be used as the potential PCM crucible in the experiments.

The purpose of this work is to experimentally investigate the effect of B addition to the phase formations of Si-B alloys and the interlayer distributions between Si-B alloys and graphite.

2. Experimental Description

2.1. The phase formation experiments of Si-B alloys in graphite crucibles.

In the current study, the materials used in the experiments were 99.9 % B powder and commercial pure solar grade Si. The effect of increasing B content in the phase formations of Si-B alloys was produced by melting them in the induction furnace. For this purpose, the B and Si powders were weighed in the amount of 4 g and melted in the dense graphite crucibles (IG-15, Tanso) with a continuous flow of argon. Four charged graphite crucibles with different B additions were placed in the bottom of the graphite holder. The Si-B alloys were heated to 1750 °C, held for 2 h, and then, cooled to room temperature.

2.2. Characterization techniques

The microstructures of Si-B samples were observed by Zeiss Supra, 55VP™ Scanning Electron Microscope (SEM) coupled with a Backscattered Electron image (BSE). The chemical compositions of samples were quantitatively or semi-quantitatively analyzed by Energy Dispersive Spectroscopy (EDS).

3. Results and discussion

3.1. The phase formation in the Si-B alloys

Figure 1 a-d show the microstructures of the Si-B alloys with the B content of 2-11 mass %. It shows that Si solid solution, SiB3, B4C, and SiC phases were formed in the Si-B alloys. In the Si-2B alloy, Si solid solution and eutectic structure (Si + SiB3) was detected. However, the formed phases were changed to be more complex in the Si-B alloys at B content of higher than 5 mass %. Si solid solution, eutectic structure (Si + SiB3), SiB3, SiC, and B4C particles were detected.

Figure 2 shows an isoplethal cross-section of Si-B-C system with a C content of 1500 ppm mass. As shown in the dotted line, the formed phases are located in the SiB3 + Si + B4C area at the B content of 2-11 mass % after solidification. However, the phases produced in the Si-2B alloy and in the Si-B alloys with the B content of higher than 5 mass % are different. The primary phase formed in the Si-2B alloy is Si during solidification. The size of Si particles increases with the decrease of temperature. Once the temperature is decreased to the eutectic point, the eutectic structure is produced from the eutectic reaction at 1385 °C, Liquid → Si + SiB6. With a further decrease in the temperature, SiB5 is transferred to SiB3 at 1270 °C. While the primary phase is SiB5 in the Si-B alloys with the B content of higher than 5 mass. It results in the formation of SiB5 particles in the solidified Si-B alloys. The most interesting aspect is that B4C phase is not detected in the Si-2B displayed microstructures, while it appears in the Si-B alloys with B content of higher than 5 mass %. Dalaker found that the addition of B to the Si-B melts would increase the C solubility in the B range of 0-2 mass % [7]. In our experiments, the B content is in the range of 2-11 mass %. It hence increases the C solubility in the Si-B alloys, leading to the formation of B4C and SiC in the Si-B alloys.

The phases in the Si-3.25B alloys were investigated by Grorud [8]. It formed phases were the same as in the Si-2B alloy. Therefore, the phases produced in the Si-B alloys with B content of lower than 3.25 mass % were simple. The phases formed in the Si-B alloys with the B content of higher than 5 mass % were SiB3, Si, B4C, and SiC.
3.2. The interlayer phase distribution between Si-B alloys and graphite

Figure 3a-d show the BSE images of the interlayer between graphite and Si-B alloys with the B content of 2-11 mass %. SiC and B$_4$C phases were observed at the interlayer. At the B content of 2 mass %, a single SiC layer was formed at the interlayer between Si-2B alloy and graphite. At the B content of higher than 5 mass %, B$_4$C and SiC layers were produced at the interface. Hiba! A hivatkozási forrás nem található. shows the result of EDS scan between the Si-8B alloy and graphite (as shown in the red arrow in Figure 3c). At the boundary from the metal region to the SiB$_3$ phase, there is a sharp decrease in the Si concentration, corresponding to an increase in the B concentration. Then, it is transferred to the metal region. At the boundary from the SiB$_3$ phase to the B$_4$C layer, the
concentration of B and C increase, and that of Si decreases. Subsequently, it is transferred to the SiC region with an increase of C and Si. In the end, Si and B contents are at a low level in the graphite. It indicates that B will be consumed to produce a B$_4$C layer at higher B content alloys.

Figure 5 illustrates the relationship between B and C in the Si-B-C system. The X and Y axes represent the B and C content, respectively. The blue line is the boundary between SiC and B$_4$C regions, where the left region is SiC, and the right region is B$_4$C. Other coloured lines show the tendency of C with the increase of B at different temperatures. It is known from the figure that C is in the form of SiC at low B content, while it is in the form of B$_4$C at high B content. Moreover, the calculated B equilibrium content with SiC and B$_4$C is 2.2 mass % at 1450 °C, 3.1 mass % at 1550 °C, 4.4 mass % at 1650 °C, and 6.2 mass % at 1750 °C.

**Figure 3.** SEM images (BSE contrast) of the microstructures of the interlayers between C-3 crucible and Si-B alloys with the B content of 2, 5, 8 and 11 mass % at 1750 °C.

**Figure 4.** Line scan of the across the interface between Si-8B alloy and graphite; 2 h at 1750 °C.
The formation of B₄C layer between Si-B alloys and graphite can be explained based on the calculation in Figure 5. Three different conditions are summarized as follows:

- If the B content is 2 mass %, which is lower than 2.2 mass %, the molten Si-2B alloy equilibrates with SiC in the temperature range of 1450-1750 °C. Therefore, there is only a continuous SiC layer formed between the Si-2B alloy and graphite, as shown in Figure 6a.

- If the B content is 5 mass %, which is in the range of 2.2-6.2 mass %, the molten Si-5B alloy equilibrates with SiC at 1750 °C. While it equilibrates with B₄C at the temperatures range of 1450-1650 °C. It means that the B₄C layer is not produced at 1750 °C, but in the cooling process. The process is shown in Figure 6b.

- If the B content is 8 or 11 mass %. The Si-B alloy equilibrates with B₄C at 1750 °C, as shown in Figure 6c.

**Figure 5.** The function of C content with increasing B content in Si-B alloys at temperatures of 1450-1750 °C.

**Figure 6.** Illustration of the interaction between graphite and Si-B alloys from 1750 °C to room temperature (a-c).
4. Conclusion
The following conclusions are obtained from the experiments in the induction furnace. The phases formed in the Si-B alloys change in the increase of B content. Si and eutectic structure (Si + SiB$_3$) are formed in the Si-2B alloy. While Si, SiB$_3$, B$_4$C, and SiC are formed in the Si-B alloys with the B content of higher than 5 mass %. The barrier layer of SiC is produced along the interface between the Si-2B alloy and graphite. SiC and B$_4$C layers are formed between graphite and Si-B alloys with the B content of higher than 5 mass %, therefore, the B$_4$C layer can be controlled by the B addition in the Si-B alloys.

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