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Carbothermal reduction process of silica formed from shirasu volcanic ash using solar furnace

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Abstract. Metallurgical grade silicon was formed using Shirasu volcanic ash as starting material with solar furnace. The solar furnace was composed of two parts: Fresnel lens and reacting furnace. The reacting furnace was composed of a cylindrical vacuum chamber and quartz glass plate functioning to guide the concentrated sunlight into the furnace, and was placed at the focal point of the Fresnel lens. The sample was made from a mixture of silica formed from Shirasu volcanic ash and carbon, and placed in the carbon crucible inside the reacting furnace. The sample was irradiated for 3 hours, and the furnace was left until it cooled down to room temperature. After the cooling process, the sample was mixed and placed in the carbon crucible, and it was irradiated and cooled with the same processes again. After the experiment, the sample was evaluated by X-ray diffraction and the production of silicon was confirmed.

1 Introduction

A kind of the volcanic ashes called “Shirasu”, abundantly deposited due to a big pyroclastic flow in the Southern Kyushu, Japan, which happened 20 to 100 thousand years ago, is one of the unused natural resources. Shirasu is unsuitable for agriculture due to excessive water drainage, and poses a heavy damage every year as sediment disaster. In order to use the Shirasu which may cause sediment disaster and serious damage to the crops, various areas had been investigated to find its promising application [1, 2]. In view of this matter, we provide the formation method of metallurgical grade silicon (MG-Si) from Shirasu volcanic ash, as a starting material.

MG-Si is used as an alloy element in steel industries and metallurgical companies. MG-Si is used for the production of solar cells and electronic devices [3]. All those products are produced on a commercial scale by conventional carbothermal reduction process. The overall reaction of MG-Si production using silica with carbon is shown by the following equation.

$$SiO_2(s) + 2C(s) = Si(l) + 2CO(g) \tag{1}$$

In industry, MG-Si is mainly produced by silica and carbon at 1900°C [4]. It is an energy intensive process.
In recent years, the interest regarding renewable energy has been growing due to the decrease in fossil fuels and the global warming. With a view of growth in the world’s population, the demand for energy is always growing, while the fossil fuel reserves, in particular oil, are in the stake of exhaustion [5]. That is why, the use of clean, safe and cost-effective energy supplies need to be increased. Solar energy which has an intensity of 1000 W/m^2, has an important role to play within this framework, as it may also be used in solar furnace application. The solar furnace is possible to produce high temperature in a short period of time by utilizing Fresnel lens as a sunlight concentrator. This method is a new production process to create materials that require to be done under high temperature condition with regards of the shortage of energy resources.

In this study, instead of requisite thermal energy, we prepared a MG-Si using the solar furnace that produced an ultrahigh temperature condition by utilizing a Fresnel lens as a sunlight concentrator. The MG-Si was prepared by silica formed using Shirasu and carbon.

2 Experimental procedure

The solar furnace was composed by two parts; Fresnel lens and reacting furnace. In solar thermal conversion applications, Fresnel lens has the advantages of small volume, light weight, suitable for mass production at low cost, and effectively increasing the energy density. The material of the Fresnel lens was PMMA, and it had an area of 1.40 m × 1.05 m. Figure 1 shows the concentrator system and the schematic of the reacting furnace. The reacting furnace was composed of a cylindrical vacuum chamber (diameter: 20.3 cm, depth: 19.2 cm) and quartz glass plate functioning to guide the concentrated sunlight into the furnace, and we put a thermal insulation and crucible, at the Fresnel lens’ focal point.

The sample was made from a mixture of silica formed using Shirasu volcanic ash [6, 7] and carbon, and

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placed in the carbon crucible, as shown in Fig. 2, inside the reacting furnace.

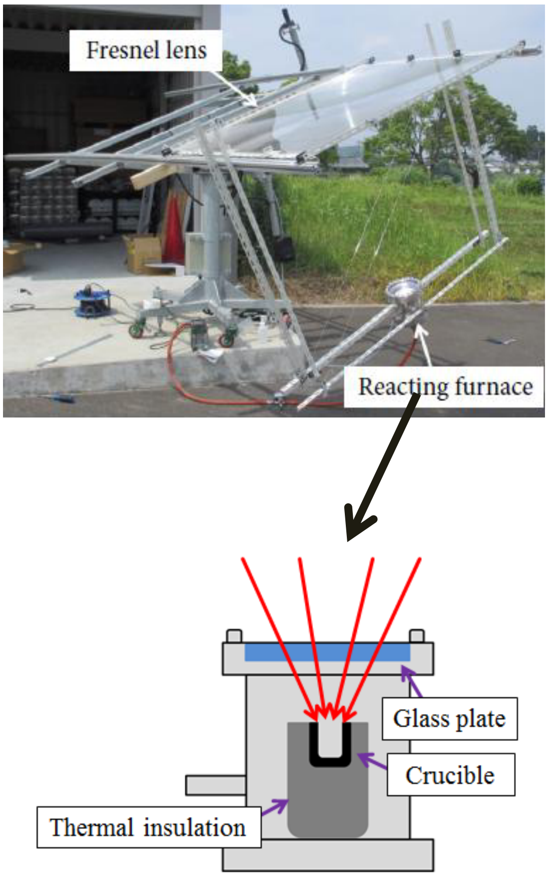

Figure 1. Concentrator system and schematic of the reacting furnace.

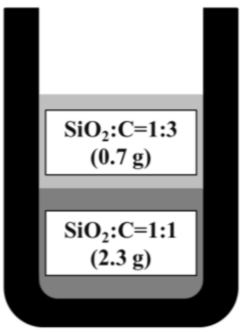

Figure 2. The sample ratio in crucible.

In order to form silica from Shirasu, the materials (Shirasu: 59.6wt%, Li_2Co_3: 4.8wt%, B_2O_3: 23.5wt%, MgO: 5.3wt%, $CaCO_3$: 4.4wt%, Na_2CO_3: 2.4wt%) were mixed using blender for 3 minutes. The resultant powder mixture was placed into a platinum (Pt) crucible and was melted at 1400°C for 3 hours in an electric furnace. The mother glass was formed by quenching the melt in pure water. The bulk particle sizes were adjusted to be less than 1 mm in diameter. Leaching was performed by immersing the mother glass into 1 M hydrogen chloride (HCl) solution at 90°C for 4 hours in total; tha acid solution was refreshed after immersing the mother the glass for 2 hours. The silica was then washed with deionized water and dried.

In the actual process of the MG-Si formation, three reactions take place,

$$SiO_2(s) + C(s) = SiO(g) + CO(g) \quad (2)$$
$$SiO(g) + 2C(s) = SiC(s) + CO(g) \quad (3)$$
$$SiO(g) + SiC(s) = 2Si(s) + CO(g). \quad (4)$$

SiO is easily produced by the reaction (2) near 1100 °C. Then SiC formation occurs through reaction (3) above 1300 °C. In the solar furnace, the upper part of the sample is irradiated with sunlight and becomes the high temperature. Therefore, the sample was prepared as shown in Fig. 2. After that, the air inside the reacting furnace was discharged so that it was in the vacuum condition. Then the Ar gas was left to flow into the reacting furnace until it reaches 0.1 MPa. Next, the sample was irradiated with high concentrated sunlight for 3 hours. While the Ar gas kept on flowing at 2 L/min into reacting furnace. After the irradiation process, the furnace was left until the sample was cooled down to room temperature under Ar atmosphere. The sample was mixed, and placed in the carbon crucible, and was irradiated in the same way again for 3 hours, and was cooled down to room temperature.

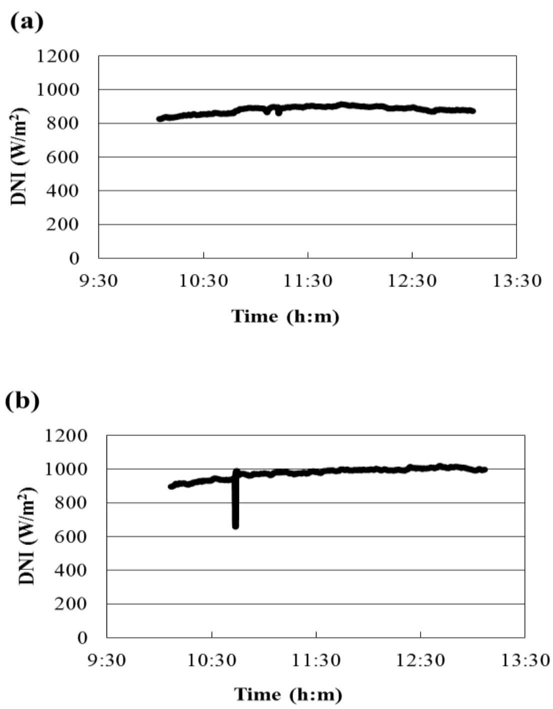

Figure 3. Direct normal irradiance (DNI) during the (a) first and (b) second irradiation processes.

Fig. 3(a) and (b) shows the direct normal irradiance (DNI) during the first and second irradiation processes, respectively. DNI was stable and high with approximately 900 W/m^2 and 1000 W/m^2 during the experiment. The solar furnace system uses the Fresnel lens to collect sunlight and focuses it onto the reacting chamber. The system can only use the direct beam component of sunlight. Since the solar furnace is equipped with the sun tracking system, temperature of the furnace depends on the intensity of DNI. Therefore, it is necessary to irradiate the sample using a stable and high DNI. Finally, the sample was evaluated by X-ray diffraction (XRD, PANalytical, X'Pert PRO).

3 Results and discussion

Fig. 4(a) and (b) shows the image of the sample inside the inner carbon crucible after first and second irradiation process, respectively. From the figure, it was confirmed that the dent ("Irradiated portion") was formed on the sample, where the highly concentrated sunlight hit. At the portion in the Fig. 4(a), green material and glass lump was formed. On the other hand, at the portion in the Fig. 4(b), green and black material was formed. This particular part ("Irradiated portion") of the samples were analyzed using XRD.

Fig. 5(a) and (b) shows the result of XRD pattern of the sample after first and second irradiation processes, respectively. The result of XRD pattern analysis in the Fig. 5(a) showed that the silica, carbon and SiC diffraction peaks were appeared. From the XRD result, the sample was found to have produced no Si. On the other hand, the result of XRD pattern analysis in the Fig. 5(b) showed that the SiC and other four diffraction peaks were appeared. The four diffraction peaks that labeled with (111), (220), (331) and (422) were considered as the characteristic of Si. From the XRD result, the sample was found to have produced the Si.

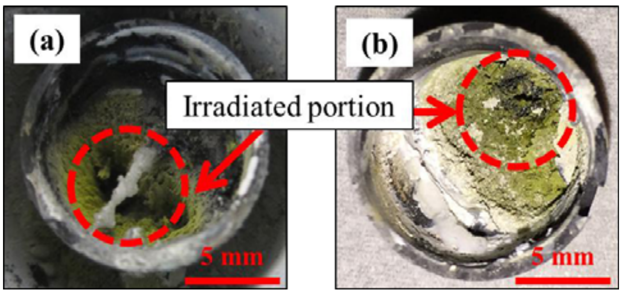

Figure 4. Image of sample inside the crucible after (a) first and (b) second irradiation process.

In the previous study, we have successfully prepared MG-Si from silica and SiC, which were formed from Shirasu volcanic ash, using the solar furnace [8]. DNI at that time was approximately 900 W/m^2. In the case that carbon was used as the reducing agent, the Si wasn't formed at 900 W/m^2. However, the Si was formed after the second irradiation process. This is because SiC was generated and carbon disappeared in the sample by the first irradiation.

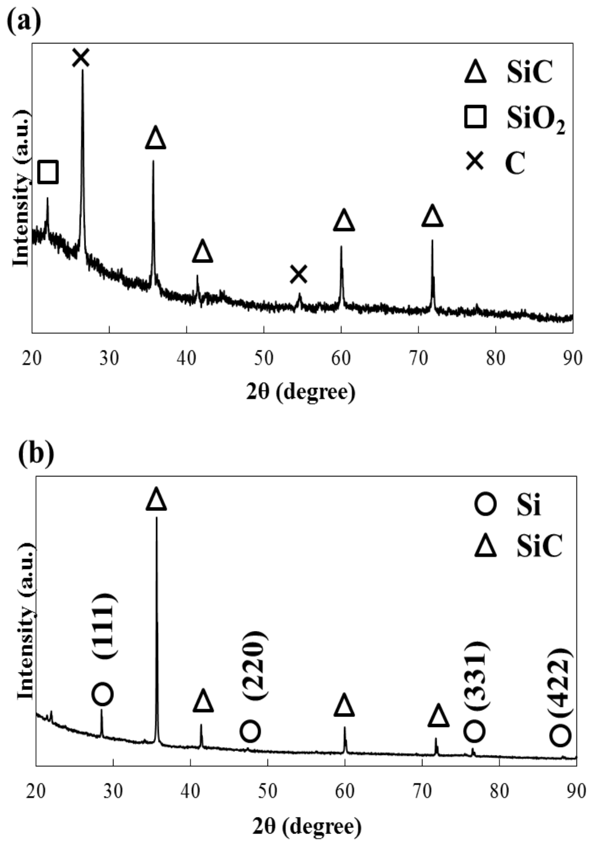

Figure 5. X-ray diffraction pattern of the sample after (a) first and (b) second irradiation processes.

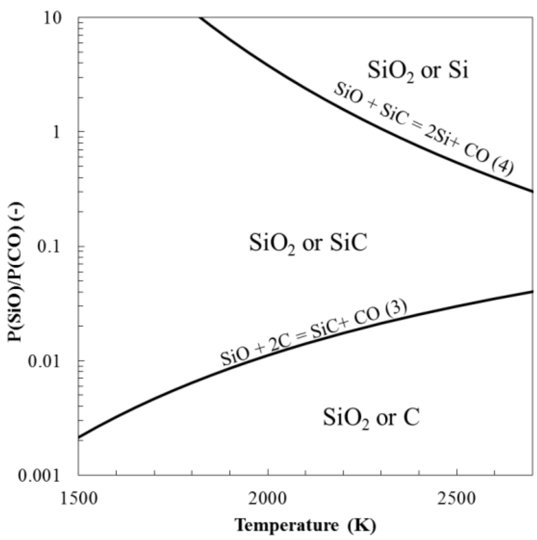

Figure 6. Phase diagrams of the silica reduction process.

Fig. 6 shows the phase diagram of the silica reduction processes with carbon calculated using data reported by Nagamori et al. [9]. The phase diagram indicates that reaction (3) is easier than the reaction (4). If SiO_2 and C exist in the reaction system, reaction (3) takes place preferentially.

4 Summary

We have successfully prepared Si from silica, which were fabricated from Shirasu volcanic ash, and carbon using the solar furnace. The solar furnace was composed by two parts; Fresnel lens and reacting furnace. The material of the Fresnel lens was PMMA, and it had an area of 1.40 m × 1.05 m. The reacting furnace was composed of a cylindrical vacuum chamber (diameter: 20.3 cm, depth: 19.2 cm) and quartz glass plate functioning to guide the concentrated sunlight into the furnace, and we put a thermal insulation and crucible, at the Fresnel lens' focal point. The sample was made from a mixture of silica formed using Shirasu volcanic ash and carbon, and placed in the carbon crucible inside the reacting furnace.

The Si was formed after the second irradiation process. In order to form Si after the first irradiation process, higher DNI or SiC as the reducing agent will be necessary. The method implemented in this study could effectively avert the shortage of energy resources in contrast to the traditional process for the formation of Si. This method is expected to be the valid utilization method of Shirasu volcanic ash as a natural resource and to form superior materials using renewable energy.

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