Formation of Silicon from Shirasu Volcanic Ash Using Solar Furnace

K. Hatakeyama, H. Kaneko, and K. Nishioka

***Abstract*—Silicon was prepared from Shirasu volcanic ash using solar furnace. The solar furnace was composed from two parts; Fresnel lens and reacting furnace. Fresnel lens was used to concentrate sunlight onto the reacting furnace where the sample was put on. The sample was made from silica and silicon carbide formed using Shirasu volcanic ash, and placed in the carbon crucible inside the reacting furnace. By using light of sun concentrated with Fresnel lens, the sample was irradiated for 3.5 hours and the furnace was left until it cooled down to room temperature. Both irradiating and cooling processes were done under argon atmosphere. After the experiment, the sample was evaluated by X-ray diffraction. The sample was found to have produced the Si component.**

***Index Terms*—Silica, silicon, solar furnace, volcanic ash.**

I. 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 a sediment disaster. In order to use Shirasu which may causes 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 of silicon (Si) from Shirasu volcanic ash, as a starting material.

Si is used as an alloy element in steel industries and metallurgical companies. 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 processes. The overall reaction of Si production using silica with carbon is shown by the following equation.

$$SiO_2(s) + 2C(s) = Si(s) + 2CO(g) \quad (1)$$

In industry, Si is mainly produced by silica and carbon at 1900 ℃ [4]. It is an energy intensive process. To produce at low cost, Wang, *et al.* reported the reaction of silica with aluminum metal at 1480 ℃ [5]. And Bao, *et al.* also reported magnesiothermic reduction process at 650 ℃ [6]. In this way, there are many studies to produce Si at low cost.

On the other hand, 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 of oil, are in the stake of exhaustion [7]. 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. Through this method, a new production process to create materials that require to be done under high temperature condition with regards of the shortage of energy resources has been significantly provided [8]-[11].

In the actual process of the 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 ℃. Then SiC formation occurs through reaction (3) above 1300 ℃. Estimation of Gibbs free energy (ΔG) indicates that reaction (4) takes place above 1700 °C, but ΔG of reaction (3) is lower than that of the reaction (4). If SiO_2 and C exist in the reaction system, reaction (3) takes place preferentially [12]. In view of this matter, we provide the formation of Si by silica and SiC fabricated using Shirasu.

In this study, instead of requisite thermal energy, we prepared a Si using the solar furnace that produced an ultrahigh temperature condition by utilizing a Fresnel lens as a sunlight concentrator. The Si was prepared by silica and SiC formed using Shirasu. There is no report which forms the semiconductor material of high value like Si by using environment-friendly concentrated sunlight. We prepared a Si using the solar furnace that produces an ultrahigh temperature condition by utilizing a Fresnel lens as a sunlight concentrator.

II. Experimental Procedure

Fig. 1 shows the solar furnace created in this study. 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 productions 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. Fig. 2 schematically shows the reacting furnace. The reacting furnace was composed of a cylindrical vacuum chamber

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(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.

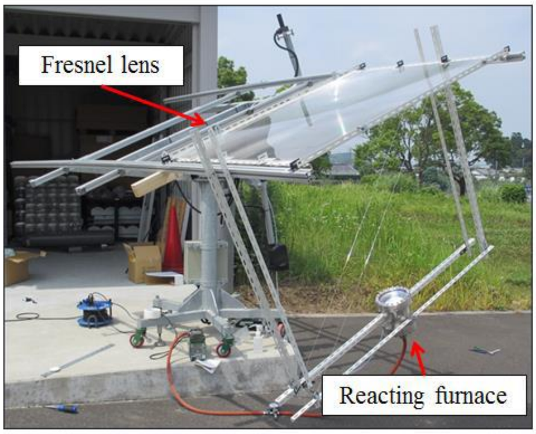

Fig. 1. Solar furnace system.

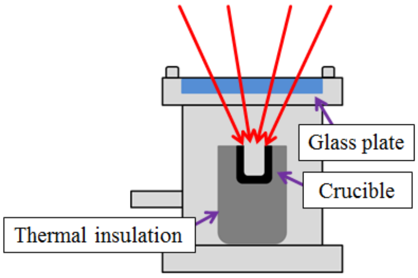

Fig. 2. Schematic of reacting furnace.

The sample was made from a mixture of silica formed using Shirasu volcanic ash [13], [14] and SiC fabricated using silica and graphite [15], and placed in the carbon crucible inside the reacting furnace. The high purity nanoporous silica was fabricated using Shirasu volcanic ash as a starting material. The materials with Shirasu were melted at 1400 ℃. A mother glass was formed by quenching the melt in pure water. Leaching was performed by immersing the mother glass into an HCl solution. Non-silica phases formed by phase separation in the mother glass were leached out with acid solution. The obtained porous silica was more than 99% pure [13], [14].

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 the high concentrated sunlight for 3.5 hours at about 2000 ℃. The temperature at the focal point was measured by the Infrared Radiation Thermometer (CHINO, IR-CAS2) at 11 AM of 27 November 2014. Figure 3 shows the direct normal irradiance (DNI) during the experiment. The circle of the Fig. 3 shows the time when we measured the temperature using the Infrared Radiation Thermometer. DNI was stable and high with approximately 890 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. The reason of the drop of DNI in Fig. 3 was temporal cloudiness. 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 in order to avoid oxidization of the carbon crucible. Finally, the sample was evaluated by X-ray diffraction (XRD, PANalytical, X'Pert PRO).

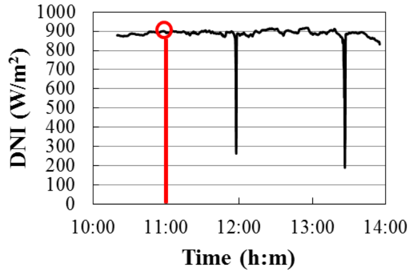

Fig. 3. Direct normal irradiance (DNI) during the experiment.

III. Results and Discussion

Fig. 4 shows the image of the sample inside the carbon crucible after the irradiation process. From the figure, it was confirmed that the dent ("Irradiated portion" in the Fig. 4) was formed on the center of the sample, where the highly concentrated sunlight hit. This particular part (irradiated portion) of the sample was analyzed using XRD.

Fig. 5 shows XRD pattern of the sample after the irradiation process. The results of XRD analysis showed that the silica and SiC, which were prepared by using Shirasu volcanic ash, and other three diffraction peaks were appeared. The three diffraction peaks that labeled with (111), (220) and (311) were considered as the characteristic of Si [16]. From XRD results, the sample was found to have produced the Si component. However, the Si peak that labeled with (111) is weaker than the SiC (111) peak. The sample included a small amount of Si.

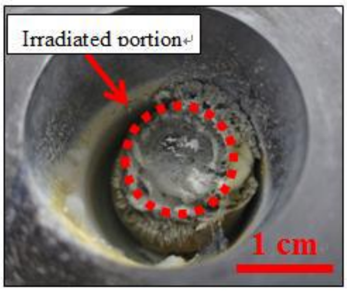

Fig. 4. Image of sample inside the carbon crucible.

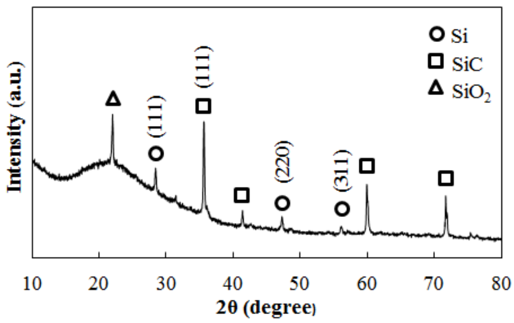

Fig. 5. X-ray diffraction pattern of the sample after irradiation.

Fig. 6 shows the image of the scaffolding on the furnace wall after the irradiation process. The color of the scaffolding was yellow. The large quantity of the scaffolding was obtained every experiment. The scaffolding was analyzed using XRD.

Fig. 7 shows XRD pattern of the scaffolding after the irradiation process. The results of XRD analysis showed that the silica and other three diffraction peaks were appeared. The three diffraction peaks that labeled with (111), (220) and (311) were considered as the characteristic of Si. From XRD results, the sample was found to have produced the Si component. There was no peak of SiC. It is considered that a chemical vapor deposition occurs in the reacting furnace. SiO and carbon gases generated by the reaction of the sample inside the carbon crucible and high temperature produced Si on the furnace wall.

Fig. 6. Image of the scaffolding on the furnace wall after the irradiation process.

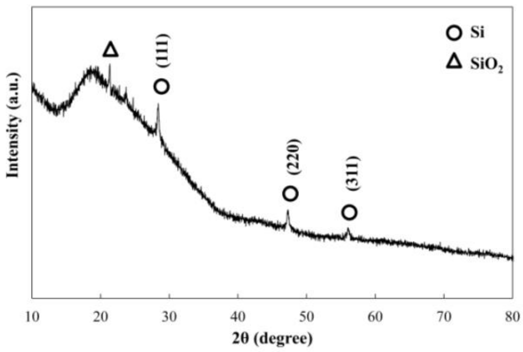

Fig. 7. X-ray diffraction pattern of the scaffolding on the furnace wall after the irradiation process.

IV. Conclusion

Silicon was prepared from Shirasu volcanic ash using 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 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 from Shirasu volcanic ash and SiC fabricated using silica and graphite, and placed in the carbon crucible inside the reacting furnace.

We have successfully prepared Si from silica and SiC, which were fabricated from Shirasu volcanic ash, using the solar furnace, never been performed before. However the sample included a small amount of Si. In order to form a large quantity of Si, the longer irradiation time 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, to form superior materials using renewable energy.

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