Optimization of the Granulation Binders of High-Purity Carbothermic Reduction for Solar-Grade Silicon

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The direct carbothermic reduction process from high-purity silica is promising for next-generation low-cost silicon solar cells. In this process, the granulation process is essential to avoid blowout of the silica powder. In this study, we investigated the effect of binders on this reduction process using four kinds of binders. The real-time monitoring of the chamber pressure and quadrupole mass spectroscopic analysis indicated the sign of the blowout phenomena of the generated CO gas and decomposition gas of the binders. In the case of starch and sucrose, the strengths of granules were not enough to the process with the pressure of the generated CO gas, while the granules with enough strength, namely, the ones with polyvinyl alcohol (PVA) and carboxymethyl cellulose (CMC), resulted in silicon yield of 33.8% and 27.8%, respectively.

Keywords: solar-grade silicon, carbothermic reduction, powder granulation, polyvinyl alcohol, carboxymethyl cellulose

1. Introduction

Silicon is the major element used in electronic devices and solar cells. The challenge and focus to reduce its production costs and fulfill the demand for solar cell applications have increased recently.¹ Various routes of Si production have been investigated, including the Siemens, Union Carbide, and fluidized bed processes² and electrolytic production.³ For the production process of solar-grade silicon (SoG-Si) with a purity of 6N or higher, some reduction processes have multiple reduction processes with high temperature treatment. The energy cost of these reduction processes depends on the count of high temperature processes in the total process. The omission of the processes with high temperature treatment leads to the suppression of the total cost. The Siemens process, which is the current process for SoG-Si production and is shown in Fig. 1, possesses two reduction processes: the first is the reduction process using the carbon reductant, and the second is the reduction of SiHCl₃ gas using hydrogen gas.⁴–⁷ The high-purity carbothermic reduction process, which is the new candidate process for a low-cost SoG-Si process, is the direct reduction process involving reduction of purified silica powders by wet chemical process.

The direct reduction process is suitable for the large-scale mass production of SoG-Si because it consists of only one reduction process with high temperature treatment. The form of the silica purified by wet chemical process is not lump but powder.⁸ The chemical reactions using raw materials in powder form frequently cause small explosions owing to the absorbed and generated gases.⁹,¹⁰ Therefore, pelleting or granulation processes are essential for the chemical reaction of powder sources. In some previous reports related to the carbothermic reduction of silica, small amounts of substances such as demineralized water¹¹, a small amount of aqueous starch,¹² and sucrose¹³ were used as binders to agglomerate silica and carbon powders. However, the selection guide for suitable binders in the carbothermic reduction process is still not clear.

In the present study, we investigated the effect of binders on the Si yield of the carbothermic reduction process. The properties of the granules made with polyvinyl alcohol (PVA), carboxymethyl cellulose (CMC), starch, and sucrose were compared.

2. Materials and Methods

2.1 Granulation process

The desired attributes of the product granules are controlled by a combination of formulation design (the feed pow-
ders, binders, and added liquids) and process design (the type of granulator and the operating parameters). In various granulation methods, rolling granulation, which belongs to the category of wet granulation, has the merits of easy control of the grain size, protection from contamination, and a high yield of granules.

A pan-type granulator with a dry heating system (AS ONE Corporation, Japan) was used for granulating the feed powders in the present study. The feed powders for all granulation processes were prepared by mixing silica (diameter 20–100 µm, Taiheiyo Cement Corporation, Japan) and glassy carbon (diameter 20 µm, Tokai Carbon, Ltd.).

In the present study, four kinds of binders were used: polyvinyl alcohol (PVA) \([\text{CH}_2\text{CH} (\text{OH})_n]\) (Kuraray Co., Ltd., Japan), carboxymethyl cellulose (CMC) \([\text{CH}_2\text{COONa}]_n\) (Wako Pure Chemical Industries, Ltd., Japan), starch \([\text{C}_6\text{H}_{10}\text{O}_5]\) (Wako Pure Chemical Industries, Ltd., Japan), and sucrose \([\text{C}_12\text{H}_{22}\text{O}_{11}]_n\) (Kanto Chemical Industries Co., Inc., Japan).

The binders were added to a 170 g mixture of SiO2 and C, with a ratio of 3% by weight for PVA and CMC, 6% by weight for starch, and 10% by weight for sucrose. The small differences in the weight ratios of the binder were due to the presence of residuals in the agglomerates of the powders. The mixed powder was supplied to the granulator, and then pure water was sprayed on the mixture while rotating the tilted pan for approximately 10 minutes. After stopping the rotation, the granules were dried at 70°C for 2 hours in the pan.

### 2.2 Reduction process

The reaction mechanism of the carbothermal reduction of SiO2 by carbon is shown in eqs. (1)–(6):

\[
\begin{align*}
\text{SiO}_2 + \text{C} & \rightarrow \text{SiO} + \text{CO} \\
\text{SiO}_2 + 3\text{C} & \rightarrow \text{SiC} + 2\text{CO} \\
2\text{SiO}_2 + \text{SiC} & \rightarrow 3\text{SiO} + \text{CO} \\
\text{SiO} + 2\text{C} & \rightarrow \text{SiC} + \text{CO} \\
\text{SiO} + \text{SiC} & \rightarrow 2\text{Si} + \text{CO} \\
\text{SiO}_2 + \text{Si} & \rightarrow 2\text{SiO} 
\end{align*}
\]

The above set of equations indicate that Si production can be reached only through the reaction of SiC and SiO represented by eq. (5). The SiO gas is generated in the reactions represented by eqs. (1), (3) and (6). The formation of SiC can occur in the reactions shown in eqs. (2) and (4). To accelerate the Si production rate, it was reported that the addition of SiC could serve as a barrier to gaseous SiO, which may lead to the acceleration of the reaction and an increase in Si formation. By means of adding SiC as the initial raw material, a partial amount of SiC is consumed in eqs. (5) and (3). To promote SiO gas and SiC efficiently under the reaction in eq. (5), the granules and SiC grains were loaded alternately into the crucible.

Figure 2 shows a schematic representation of the crucible setup in the present study. The granules and the 6H-SiC powder were alternately supplied in layers into a high-purity graphite crucible (inner diameter 70 mm, height 175 mm). The starting molar ratio of the raw powders was decided to be SiO2:C:SiC = 1:0.75:0.49 for the four types of binder. Due to the scale of our furnace, the loss of SiO gas is quite large compared to the Si product. The source of elemental Si requires a much larger ratio than the SiO2:C molar ratio of 1:2 estimated by the ideal chemical reaction, SiO2 + 2C = Si + 2CO. Before this study, we also performed the optimization of the SiO2 and C ratio for the silica reduction process in the 1/10-scale furnace, which has less of a problem with blowout of the powders. Therefore, we used the mixture molar ratio of SiO2:C = 4:3 in this study. The crucible was capped with a graphite lid with one hole of 10 mm diameter to release the generated CO gas. The whole crucible was covered with a 10 mm-thick carbon felt as a thermal insulator.

The reduction process was carried out using an induction heating furnace of 40 kW power (Toei Scientific Industrial Co., Ltd.), as shown in Fig. 3. The fundamental specification of this system is almost the same as those of our previous reports except a 10-times increase in the volume of the crucible. The evacuation system of this apparatus is composed of a rotary pump and a diffusion pump, which can reach \(10^{-3}\) Pa in vacuum. During the reduction process, a pure argon (99.999 vol%) atmosphere was maintained, with a pressure of slightly less than 1 atm (0.07 MPa), in order to avoid leakage of the lethal carbon monoxide gas; this value was fixed for all experiments. The evacuation of the chamber to a pressure of the order of \(10^{-3}\) Pa was required before filling with argon gas to remove the impurity gases, such as nitrogen, which strongly affect the gas analysis of carbon monoxide. When omitting the gas analysis by quadrupole mass spectrometry, this evacuation by the diffusion pump is not required. During the reduction, the temperatures of the top and sides of the crucible were monitored by highly sensitive 2-color type infrared thermometers with a temperature range from 500°C to 3500°C (IR-CAQ, CHINO Corporation, Japan) through the glass window of the chamber, and the chamber gas was analyzed by a quadrupole mass spectrometer. The total pressure in the reaction was monitored by a capacitance gauge. The...
quartz tube was placed in between the crucible and the induction coil for protection. The crucible was heated by the induction coil with a frequency of 30 kHz under an open-loop control.

Figure 4 shows the temperature profile curves of the blank test as a typical temperature profile measured by the infrared thermometer in the present study. Every heat experiment with the four kinds of binder was performed twice, and the reproducibility of the result was confirmed. Every instance of heating for granules was performed under the same conditions excepting the contents of the crucible. The heating time was 20 minutes and the maximum temperature at the side of the crucible was around 2100°C. The reason for the short heating time is the efficient heating method using the induction heating system and the promotion of the reaction in eq. (5) by the addition of SiC. It is noted that the thermometer cannot measure the target temperature below 463°C. The voltage and current of the induction coil, the temperatures of the top and sides of the crucible and the chamber pressure from the capacitance gauge were recorded by a data logger.

2.3 Method of analysis

The hardness (strength) of the granules was measured by a mechanical force gauge (push-pull gauge) (IMADA, LTD, Japan). The sieving was performed by a polyethylene sieve (12 mesh/2.54 cm). After reduction, the products were milled using a planetary micro mill (pulverisette 7 classic line, Fritsch, Germany). The analysis of x-ray diffraction (XRD) with a Cu-\(K\alpha\) (\(\lambda = 1.5405\) Å) radiation source over the angular range of 20° ≤ 2θ ≤ 140° and a scan rate of 10°/min was
employed by an x-ray diffractometer (SmartLab, Rigaku Corporation) to examine the phase composition. A small amount of MgO was added to the milled products as a standard material to estimate the quantity of Si and 6H-SiC in products using the following equation:

$$\frac{I_{\alpha}}{I_{s}} = k\left(\frac{X_{\alpha}}{X_{s}}\right)$$

where $I_{\alpha}$ and $I_{s}$ are the peak intensities of the sample and the MgO standard, respectively, and $X_{\alpha}$ and $X_{s}$ are the weight fractions of the sample and the MgO standard, respectively. The calibration constant $k$ is estimated from the ratio of the x-ray peak intensities of $I_{\alpha}/I_{s}$ as a function of $(X_{\alpha}/X_{s})$. The estimated values of $k$ were 3.962 and 0.656 for Si(111) and 6H-SiC(101), respectively, based on MgO(200). It is noted that the main peaks of 6H-SiC(101) have not overlapped with that of 3C-SiC(111), while the main peaks of 3C-SiC(111) have overlapped with those of 6H-SiC(101). The peaks of Si (111) and 6H-SiC (101) were chosen for the estimation of $k$.

A scanning electron microscope (SEM, Hitachi SU8010) equipped with a Horiba scientific energy dispersive spectrometer (EDS) analyzer was used for the composition analysis. EDS data was analyzed using Horiba Emax Version 2.1 software to measure the quantity of oxygen in the products, which was used to calculate the amount of SiO$_2$ in the products. The quantity of 3C-SiC was estimated using the following equation:

$$W_{3C-SiC} = W_{\text{Product}} - W_{6H-SiC} - W_{Si} - W_{SiO_2}$$

where $W_{3C-SiC}$, $W_{\text{Product}}$, $W_{6H-SiC}$, $W_{Si}$, and $W_{SiO_2}$ are the weights for 3C-SiC, product, 6H-SiC, Si, and SiO$_2$, respectively.

3. Results and Discussion

3.1 Properties of granules

Figure 5 shows the images and grain properties of granules with four different binders: PVA, CMC, starch, and sucrose. The size of the granules with PVA were larger than those with other binders, while the average bulk densities of PVA, CMC, starch, and sucrose granules were (0.88 g/cm$^3$), (0.99 g/cm$^3$), (1.18 g/cm$^3$), and (1.70 g/cm$^3$), respectively. In this granulation method, the formation of granules starts gradually by agglomeration during the rolling motion. The size of granules should be determined by competition between the force of coagulation of the binders and the collapse of grown granules by the rolling motion. The amount of water sprayed for the granulation was minimal, to avoid adhesion of granules to the wall of the pan. After drying, granules were sieved using a polyethylene sieve. From the sieve and the estimation of the adhered powder, the weight loss of the granules of the PVA, CMC, starch, and sucrose were 0.96 g, 4.55 g, 7.1 g, and 0 g, respectively. The granules with sucrose were fragile during handling and broke into powders eventually.

Figure 6 shows the hardness of the granules as a function of the binder weight ratio with the standard deviation. The hardness was estimated by the force required for crushing the selected granules (which were an average of approximately 10 mm)
4 mm in diameter). The required crushing force has a direct linear relationship with the increasing weight ratio of the binders. This relationship is consistent with the previous report. Compared to the granules with PVA, CMC, starch, and sucrose, the granules with PVA showed a higher strength, and the required force for crushing CMC and starch granules was saturated by the increase in the binder ratio. Possible reasons for this difference in the hardness of the granules can be the degree of polymerization of the binders and the bulk density of the granules. However, in this study, it is difficult to discuss the relationship between these properties of the binders and the hardness of the granules. The investigation of the relationship will be useful for prospective improvement in the hardness control of the granules.

3.2 Reduction results
3.2.1 Chamber pressure and gas analysis

The pressures of the furnace chamber in the case of granules with the four binders and with only powder as a starting material were measured. In the case of powders without the granulation, several explosions in the crucibles were observed during heating because of the large amount of gas absorbed on the large surface area of the powders. The explosion caused the loss of raw materials and an increase in the pressure of the chamber due to the release of the absorbed gas on the surface of the powders.

Figure 7 shows the pressure as a function of the elapsed time during the heating. The region under high temperatures of more than 1000°C is in the crucible. The volume of the crucible is 0.9 liters and that of the chamber is 432 liters. The pressure of the chamber is not affected much by the thermal expansion of the gas. The pressure sensor can only detect the generation of CO gas and the steep change of the gas emission such as the blowout of CO gas. In the case of PVA and CMC, the pressure curves change moderately. In the case of the sucrose binder and powders without the granulation, a steep increase in the chamber pressure was observed. In the case of starch, a small blowout of pieces of the raw material was observed, but only a very faint change in the pressure gauge appeared. Thus, these results indicate that the observed explosions originated from the steep release of absorbed gas on the raw materials. The chamber pressure in the case of the PVA is a bit higher than that of the CMC case for the full duration of heating.

Figure 8 shows a comparison of the quadrupole mass spectra among the experiments with PVA, CMC, and mixed powder without binder. In the case of PVA and CMC, additional peaks related to the hydrocarbon fragments (shown by arrows in the graphs) were observed. However, these peaks were not observed in the spectrum of the mixed powder. In the case of PVA, these peaks were larger than those of the CMC. This result supports the assumption that the additional pressure in the case of PVA originated from the decomposition of the binders. Because it is difficult to analyze hydrocarbons from the pyrolysis of the binders due to fragmentation at the ionization part of the quadrupole mass spectrometer, the peaks...
ratio of Si element of products and Si element of input, that is, granules and SiC powder. In the case of PVA and CMC, the Si product yield was 23.7% and 23.6%, respectively. The fact that both Si product yields indicated similar values implies a similar weight loss was caused by the escape of the SiO gas. On the other hand, the Si product yield of the obtained product in the cases of starch and sucrose were 15.2% and 11.2%. In the cases of starch and sucrose, a kind of explosion during the reduction process occurred due to the weak strength of their granules, causing loss of their raw materials.

### 3.2.2.2 Quantification of products

In the present study, it is necessary to focus only on the experimental results of PVA and CMC for product analysis because the precise discussion of the products should be limited to the results where no explosions happened. Figure 10 shows an image of the products in the case of PVA and CMC, respectively. Unreacted SiO$_2$ was not observed in the PVA product, while a formation of colorless glass-like SiO$_2$ nuggets (indicated by the arrows in Fig. 10) was observed in the case of CMC. This indicates that the reduction of silica in the case of CMC was incomplete. It is still unknown why SiO$_2$ powder scattered in the granules was condensed into glass-like nuggets in the CMC product. The understanding of this question will be useful for selection of the binder. Figure 11 shows the powder diffraction patterns by the x-ray of the milled products. In both the cases of PVA and CMC, the XRD patterns show that the main contents of the products were silicon. The products included two phases of silicon carbide, which are 6H-SiC and 3C-SiC. There was no clear peak mapped to the silica in both XRD patterns. The silicon related peaks in the PVA product were higher than those of CMC. The overall equation to calculate the weight fraction and yield is explained in previous works$^{11,21}$ and it is presented in eq. (9).

$$a\text{SiO}_2 + b\text{C} + c\text{SiC} = d\text{Si} + e3\text{C-SiC} + f6\text{H-SiC} + g\text{SiO}_2 + h\text{SiO} + k\text{CO} + l\text{C}$$

$$h = a + c - d - e - f - g$$

$$W_{\text{CO}} = W_{\text{LostGas}} - h \times 44$$

The carbon content was not considered in the products because, in this case, we have not ground the crucible as in previous works$^{11,21}$ and the focus was only on silicon products that we extracted from the crucible bottom. Silicon yield, 3C-SiC, 6H-SiC, and SiO$_2$ yields were estimated by eqs. (12), (13), (14), and (15), respectively. These equations are based on the fraction of the number of moles of each produced element and the number of moles of SiC and SiO$_2$ in the reactants.

$$W_{\text{Si}}(\%) = \frac{d}{a + c} \times 100$$

$$W_{\text{SiC}} = \frac{e}{a + c} \times 100$$

$$W_{6\text{H-SiC}}(\%) = \frac{f}{a + c} \times 100$$

### 3.2.2 Product analysis

#### 3.2.2.1 Mass balance

Table 1 shows the mass balance, the amount of input raw materials, and the output of products in the case of each of the four binders. The weight loss in the granulation and sieving processes causes the slight difference in the input weight. The ratios of lost and remained binders were estimated by another additional experiments, which is the heating of only the binder at 1750°C and the measurement of the weight of the remained product. The Si product yield is defined as a molar

Fig. 8  The mass spectra of the chamber gases during the heating in the case of (a) PVA, (b) CMC, and (c) without granulation. Data acquired from the quadrupole mass spectrometry during the reduction reveal that PVA is highly degradable; arrows show the difference in released gases.
Figure 12 shows the yield after quantification and the calculation results. The experiment with PVA granules shows a high amount of silicon with a yield of 33.8% and 27.8% in the CMC case. The value in the case of PVA is almost the same or a bit higher than that of previous similar reports without binders.\(^{11}\) Table 1 shows the summary of the total weight of products to estimate the SiO loss from the reactions. The result suggests that the loss of the SiO gas was strongly related to the decrease in silicon yield. In the case of CMC, SiO\(_2\) nuggets of 1.76 g in weight remained. The phase of 3C-SiC is formed around 1500°C, and the phase of 3C-SiC starts to change to the phase of 6H-SiC over 2100°C.\(^{22,23}\) In the present study, the temperature can be estimated to be more than 2100°C in the inner bottom of the crucible. The separation of Si and SiC can be performed by solidification of the products.

The decrease in the yield of CMC compared to PVA seems to be related to the existence of the unreacted SiO\(_2\) nuggets. The remarkable difference between PVA and CMC is the difference in their molecular structures and the sodium content. The CMC powder contains Na because it is obtained as sodium salt. The remaining char from the heating of the binder PVA and CMC is quite different, 2.4% for PVA\(^{24}\) and 35% for CMC.\(^{25}\) Therefore the basic possible origins of the difference in the yield are: (1) the effect of remained binders by heating, or (2) the generated gases from the binders. In our

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W_{\text{SiO}_2}(\%) = \frac{g}{a + c} \times 100 \tag{15}
\]

Fig. 9 (a), (b), (c), (d), and (e) Graphs presenting the variation of released gases (CO\(_2\), H\(_2\), H\(_2\)O, O\(_2\), and CO, respectively) during the reduction process analyzed by quadrupole mass spectrometry. The high degradation occurs in the PVA case in form of different gases, especially in H\(_2\)O.
preliminary data in another furnace, the formation of colorless glass-like SiO₂ nuggets was found to increase by adding the Na element in the raw materials. After systematic experiments of Na effect on the carbothermic reduction, the detail results will be discussed elsewhere.

4. Conclusion

Silicon was successfully obtained in a small-scale graphite crucible in an induction heating furnace using granules of purified silica and carbon powders. The strength of the granules to withstand outgas during heating was crucial in suppressing explosions and PVA granules showed a high strength, and its strength depended on the ratio of the adding binder in the granules. Starch and sucrose granules were fragile and they caused a low silicon yield due to small explosions of the CO gas during heating. The avoiding of the explosion requires the strength of the granules (the crushing force > 8 N). The yield of silicon production in the case of PVA was about 33.8%, while that in the case of CMC was 27.8% due to significant loss of SiO gas and the formation of glass-like SiO₂ nuggets in case of CMC.

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Fig. 11 X-ray diffraction (XRD) patterns for the products in the cases of PVA and CMC.

Fig. 12 Yield of Si, 3C-SiC, 6H-SiC and SiO₂ in sample (a) with PVA and (b) with CMC. A high yield of Si is produced in sample (a) where PVA was used compared to the CMC sample.