Magnesiothermic Reduction of Silicon Dioxide to Obtain Fine Silicon Powder in Molten Salt Media: Analysis of Reduction Mechanism

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ABSTRACT

Semiconductive silicon is widely used in solar cells, thyristors, and other important application. However, smelting and refining Si from silicon dioxide (SiO₂) still require a large amount of energy, particularly for the reduction of SiO₂ and removal of impurities. In this work, we designed an approach to prepare very fine Si powder from crystalline and/or amorphous SiO₂ through the magnesiothermic reduction of SiO₂ in molten salts. Moreover, the mechanism of reduction below 1273 K was elucidated. The composition of molten salts and the reaction temperature were varied, and their effect on the Si yield was investigated. The yield was lower in the molten NaCl-MgCl₂ molten salt solvent than in LiCl-MgCl₂, likely because of the Mg₂Si by-product formation. The higher yield in LiCl-MgCl₂ resulted from the better solubility of Mg in this molten salt and the suppression of Mg₂Si formation.

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1. Introduction

Silicon, which is one of the most abundant elements in the earth's crust, is a known high-quality semiconductor material. Moreover, unique optical and electrical properties^{1–3} have been found when controlling the assemblies or arrays of Si (e.g., nanoparticles and porous materials). According to these properties, silicon materials are expected to be useful for bioimaging^{4,5} and for the anode in Li-ion batteries.⁶ Thus far, silicon is mainly obtained from the carbothermic reduction from silica (SiO₂) at elevated temperatures, 1673 to 2273 K.⁷ There are, however, important disadvantages in this method. First, it requires substantially high temperatures, which are achieved using an electric arc furnace. Additionally, it generates large amounts of CO₂ and thus has a high environmental burden. It is therefore necessary to develop more effective methodologies for SiO₂ reduction, at lower temperatures and without using a reducing agent different from carbon (e.g., electrochemical reduction in molten salts and metallothermic reduction).^{8–10} For the production of bulk silicon, magnesium reduction presents certain advantages and is an alternative method to carbothermic reduction. To manufacture silicon in a particular shape or assembly, such as those mentioned above,^{1–6} magnesium reduction may also be an alternative method.

Magnesiothermic reduction^{11–16} is described as follows:

This reaction has been extensively studied because magnesium has a low melting point of approximately 923 K and it also has high reducibility. Additionally, the change in Gibbs energy, $\Delta_r G^\circ$, for Reaction (1) at 1073 K is calculated at -251.300 kJ/mol .¹⁷ The use of magnesiothermic reduction for the manufacture of functional Si materials, such as nanoparticles,^{12,13} thin films,¹⁴ and porous materials,^{15,16} is continuously increasing because of the moderate temperatures required for direct reduction of SiO₂ (923–1173 K). However, SiO₂ may react with Mg or MgO and form undesired products (Mg₂Si, Mg₂SiO₄, etc.).^{6,18} In particular, Mg₂Si results from the following reaction:

$\Delta_r G^\circ$ for Reaction (2) at 1073 K is estimated at -322.865 kJ/mol .¹⁷

This value is lower than that of Reaction (1), and thus Reactions (1) and (2) occur at the same time.¹⁵

In most of the magnesiothermic reduction processes, Mg gas is used as the reducing agent. Contrastingly, Liu et al.¹² obtained Si nanoparticles through magnesiothermic reduction in molten LiCl-KCl or molten NaCl-MgCl₂. Since the reduction is carried out in the liquid phase and the molten salt bath can suppress the evaporation of Mg, this method may be favorable for the production of fine Si powders. Moreover, it has been expected from the previous researches^{12,19} that the dissolution of Mg into molten salts probably contributes to the increase of the yield of Si. However, compared with the reduction process using Mg gas, the process in molten salt has been thoroughly examined and the by-product in each stage has not been analyzed. Detailed information for the following three points should be considered: the use of SiO₂ powders with a micrometer size instead of a nanometer size, the formation mechanism of by-products, and the reactivity of SiO₂ powders with Mg dissolved in molten salts.

In the present work, magnesiothermic reduction of SiO₂ powders with a micrometer size was performed in molten NaCl-MgCl₂ and LiCl-MgCl₂. The reaction products were analyzed using X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). From these results and from the thermodynamic data from the literature,^{17,20} the by-products were identified and the reduction mechanism for Si formation was inferred.

2. Experiment

2.1 Preparation and characterization of raw materials

Two different molten salt solvents (MSs) were used: an equimolar NaCl-MgCl₂ melt, as proposed by Liu et al.¹² and an equimolar LiCl-MgCl₂ melt that has higher Mg solubility than NaCl-MgCl₂ melt.¹⁹ NaCl (~99.5%, Wako Pure Chemical Industries, Ltd.) and LiCl (~99.0%, Wako Pure Chemical Industries, Ltd.) were dried under vacuum at a temperature of 50 K below their melting points, and then they were melted under a dry Ar atmosphere and individually solidified. The chemicals were mixed with MgCl₂ (approx. >99.5%, Toho Titanium Co., Ltd.) to achieve the desired compositions, melted again, and then rapidly quenched

to obtain good homogeneity. A crystalline SiO_2 powder (JIS Special Grade: >99.5%, Wako Pure Chemical Industries, Ltd.) was used as a starting material, and Mg powder (~98.0%, Wako Pure Chemical Industries, Ltd.) was used as the reductant. SiO_2 powders were ground using a planetary-type ball mill with a tungsten carbide pot, in order to investigate the effect of different powder states and particle sizes on the reactivity. XRD was used to determine the state of the SiO_2 powders after different milling times: after 1 h (SiO_2 -cryst1) and 5 h (SiO_2 -cryst5), the powder was crystalline; after 18 h, it was amorphous (SiO_2 -amorph). The specific surface areas of the SiO_2 powders was evaluated using the Brunauer-Emmett-Teller (BET) method²¹ through nitrogen absorption at 77 K using BELSORP-max instrument (BEL Japan, Inc.).

2.2 Reduction of SiO_2

Raw MS, Mg, and SiO_2 were ground and mixed using a pestle and mortar for 5 min in an argon-filled glove box at a molar ratio of $\text{SiO}_2\text{:Mg} = 1\text{:}2.2$ and a weight ratio of $(\text{SiO}_2 + \text{Mg})/(\text{SiO}_2 + \text{Mg} + \text{MS}) = 0.1$. The mixtures of raw materials with the desired compositions were loaded into an alumina crucible and dried for 15 h under vacuum in a sealed quartz vessel as illustrated in Fig. 1. The dehydration temperatures were set at 673 and 763 K for NaCl-MgCl_2 and LiCl-MgCl_2 MS, respectively. The samples were heated at varying reaction temperatures at a rate of 5 K/min using an electric furnace under Ar gas flow and kept for 5 h with Ar gas bubbling into the baths by an alumina tubes. The reaction temperatures were set at 923, 973, and 1073 K. After the reaction, the samples were quench-cooled to room temperature and then washed several times. The products were identified at each step according to XRD (D8 ADVANCE, Bruker Corp.) using the $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15418$ nm, 40 kV, 40 mA) to investigate the reduction processes. The product was initially washed with ion-exchange treated (IE) water several times to remove the MS and then with a 2 M HCl aqueous solution to eliminate MgO. Finally, the product was cleansed with a saturated $\text{NH}_4\text{F}\cdot\text{HF}$ aqueous solution to remove the unreacted SiO_2 , and the purified Si powders were obtained. Although the solubility of Si in the $\text{NH}_4\text{F}\cdot\text{HF}$ aqueous solution is low, the washing period was set short to prevent Si from dissolving. It is worth noting that the solubility of Si was much lower than that of SiO_2 . The obtained powders were examined using SEM (JSM6510, JEOL Ltd.). The yield of Si was expressed as the ratio between the weight of the product after washing with aqueous $\text{NH}_4\text{F}\cdot\text{HF}$ and the theoretically expected Si weight from the initial amount of SiO_2 .

Figure 1. Scheme of the metallothermic reduction apparatus.

3. Results and Discussion

3.1 Characterization and effects of SiO_2 powders

Table 1 presents the crystalline state and specific surface area of the starting SiO_2 , along with the yield of Si from molten LiCl-MgCl_2 SiO_2 reduction at 973 K. Crystalline Si was obtained from every reaction. When the crystalline SiO_2 powders, SiO_2 -cryst1 and SiO_2 -cryst5, were utilized, the yield of Si increased with the increase of the specific surface area. Although SiO_2 -amorph had the largest surface area among the starting materials, the yield of Si was lower than that in SiO_2 -cryst5. SEM images of SiO_2 -cryst5 and SiO_2 -amorph and their corresponding Si powders are shown in Fig. 2. Based on the SEM analysis, the particle size of Si obtained from SiO_2 -cryst5 was almost the same as that of SiO_2 -cryst5 [Figs. 2(a) and 2(b)]. On the other hand, the particle size and aggregation state, layered aggregation, of Si obtained from SiO_2 -amorph were different from those of the starting material [Figs. 2(c) and 2(d)]. It is well-known that the SiO_4 tetrahedrons in crystalline SiO_2 are arranged in an oriented order through oxygens²² and are more randomly oriented in amorphous SiO_2 .²³ The angular uniformity of the Si-O-Si bond in crystalline SiO_2 is considered to be higher than in amorphous SiO_2 . Therefore, crystalline SiO_2 powders were sequentially reduced from the surface. Contrastingly, amorphous SiO_2 was simultaneously reduced from any direction. The unreacted SiO_2 might tend to be enclosed in aggregated Si particles, and hence the particle size of Si was almost the same as that of SiO_2 . A similar phenomenon has been previously reported by Baba et al. in the calcothermic reduction of Ta_2O_5 and Nb_2O_5 in molten CaCl_2 .²⁴ The lower yield of Si from amorphous SiO_2 indicates that the unreacted SiO_2 , which was located within the Si particles, could not adequately come into contact with the reducing agent. Consequently, the obtained Si particles were larger than the original SiO_2 particles because the reduced Si aggregated and the unreacted SiO_2 was trapped within the aggregate.

Table 1. Properties of SiO_2 powders and Si yield obtained in equimolar LiCl-MgCl_2 melt at 973 K.

Sample	State	Grinding time /h	Surface area / $\text{m}^2 \text{g}^{-1}$	Yield /%
SiO_2 -cryst1	Crystalline	1	10.3	14.3
SiO_2 -cryst5	Crystalline	5	15.4	68.6
SiO_2 -amorph	Amorphous	18	23.9	45.9

Figure 2. SEM images of (a) SiO_2 -cryst5, (b) Si obtained from SiO_2 -cryst5 in the LiCl-MgCl_2 melt at 973 K, (c) SiO_2 -amorph, and (d) Si obtained from SiO_2 -amorph in the LiCl-MgCl_2 melt at 973 K.

Table 2. Si yield (%) at different temperatures.

Temp./K	NaCl-MgCl ₂	LiCl-MgCl ₂
923	12.3	29.3
973	34.2	68.6
1073	47.8	72.8

Figure 3. XRD patterns of SiO₂-cryst5 (SiO₂) and the products obtained at 973 K in the LiCl-MgCl₂ melt. The washing solutions used to remove impurities were IE water, 2 M HCl aqueous solution (aq. HCl), and saturated NH₄F·HF solution (aq. NH₄F·HF).

3.2 The effect of the reaction temperature and reaction medium

The yields of Si from the SiO₂-cryst5 at different temperatures and MS compositions are listed in Table 2. When comparing the MSs, the yield of Si from the LiCl-MgCl₂ melt was higher than from the NaCl-MgCl₂ melt at every temperature. For both melts, the yield increased with increasing temperature. Figure 3 shows the XRD patterns of the raw SiO₂-cryst5 and the products obtained at 973 K in the LiCl-MgCl₂ melt, after several washing steps. The products prepared in the NaCl-MgCl₂ melt had similar XRD patterns to those in LiCl-MgCl₂.

As shown in Fig. 3, when only the salt components were removed with water, Mg₂SiO₄ peaks appeared in the XRD patterns, in addition to the peaks of unreacted SiO₂ and those of the generated MgO and of Si [Reaction (1)]. Mg₂SiO₄ was confirmed to be formed when MS reacted with SiO₂ even in the absence of Mg, and also formed by the reaction of Mg with SiO₂ without MS. This is because molten MgCl₂, which was used as a solvent for Mg, is very hygroscopic and easily forms MgCl₂·*n*H₂O at ambient temperature in the presence of moisture. This hydrate decomposes into Mg(OH)Cl in the range of 417 to 513 K and then into MgO at 673 K as shown in Reactions (3) and (4).²⁵

Accordingly, MgO that was produced from the reaction of MgCl₂ with absorbed moisture or from Reaction (1) reacted with SiO₂ to form Mg₂SiO₄ according to Reaction (5).

After the obtained samples were dissolved with the HCl aqueous solution to remove Mg₂SiO₄ and MgO, XRD was performed on the dried precipitates. A slight but broad hump centered at $\theta = 22^\circ$ was

observed in the XRD patterns, which is characteristic of the amorphous SiO₂ phase (Fig. 3). Since this peak disappeared after leaching with aqueous NH₄F·HF, it was assigned to amorphous SiO₂, which may derive from Mg₂SiO₄ according to Simonov et al.²⁶ and from Mg₂Si as reported by Sadique.²⁷ Mg₂SiO₄ dissolves into aqueous HCl and Mg₂Si reacts with HCl to produce SiH₄ gas [Reaction (6)]. Then, SiH₄ reacts with O₂ in the air to form amorphous SiO₂ [Reaction (7)], combusting spontaneously even at room temperature.^{28–30}

Although Mg₂Si was not detected in the XRD pattern after washing with IE water, spontaneous or sparking combustion was observed when rinsing the sample with aqueous HCl, indicating that Mg₂Si was produced in the process. Even though a small quantity of Mg₂Si was produced, its XRD pattern overlapped with the peak positions of Mg₂SiO₄ and Si, and thus the detection of Mg₂Si was difficult. The results demonstrate that the magnesiothermic reduction of SiO₂ in MS produced Si and MgO, according to Reaction (1), and Mg₂Si and Mg₂SiO₄ as by-products. In addition, Mg₂SiO₄ was produced by the impurities inevitably included in MS [Reactions (3) to (5)].

Mg solubility was reported as 0.04 mol% at 1088 K in a NaCl-MgCl₂ equimolar melt by Wypartowicz et al.¹⁹ and as 0.42 mol% at 1073 K in a LiCl-MgCl₂ equimolar melt by Bukun and Ukshe.³¹ Metallic Mg dissolves in the MgCl₂ MSs according to the following reactions:^{19,32}

Hereafter, the liquid metal Mg is referred to as metallic Mg and the Mg dissolved in MS is referred to as *metal fog* Mg; the latter is different from Mg²⁺ in MS. The chemical species existing above 923 K are likely to be SiO₂ (s), metallic Mg (l), *metal fog* Mg, and MS (l). The structure of *metal fog* Mg in the MS has yet to be elucidated, but it is proposed to exist maintaining two equilibrium states, $2\text{e}^- + 2\text{Mg}^{2+} \rightleftharpoons (\text{Mg}_2)^{2+}$ and/or $2\text{Mg}^+ \rightleftharpoons (\text{Mg}_2)^{2+}$, according to the literature.³²

For the NaCl-MgCl₂ equimolar melt, the Mg abundance would result in *metallic* Mg (l) $\gg$ *metal fog* Mg in the reaction system because of the low Mg solubility. The main reaction in NaCl-MgCl₂ would proceed on the basis of the following reactions:

where $\Delta_r G^\circ$ is, respectively, -251.300 and -322.865 kJ/mol for Reactions (10) and (11) at 1073 K as calculated from the reported values.¹⁷ In addition to Si, Mg₂Si may also be produced because these reactions proceed almost simultaneously. The amount of Mg needed to reduce SiO₂ in Reaction (11) was twice that in Reaction (10); thus, more unreacted SiO₂ remained.

For the LiCl-MgCl₂ melt, in which the solubility of Mg is higher, the amount of *metal fog* Mg is likely to be larger than in the NaCl-MgCl₂ melt. Therefore, in addition to Reactions (10) and (11), the following reaction is expected to proceed:

When the products were washed with the HCl aqueous solution, spontaneous combustion was more noticeable for the product obtained from NaCl-MgCl₂ than for the one from the LiCl-MgCl₂ melt. Hence, the reaction that uses *metal fog* Mg as a reducing agent likely prevents or suppresses the production of Mg₂Si. Since the side Reaction (11) was suppressed, the conversion ratio of SiO₂ increased, and so did the Si yield.

4. Conclusions

In this study, we developed an approach to obtain a fine Si powder from SiO₂ powder via magnesiothermic reduction in molten salts. When crystalline SiO₂ was used as the Si source, the obtained Si had a grain size similar to that of the SiO₂ powder. In contrast, when an amorphous source was used, a layered Si aggregation was obtained, with a larger grain size than that of the original SiO₂ particles. The magnesiothermic reduction in molten salts yielded Si and MgO, as well as Mg₂Si and Mg₂SiO₄. A saturated aqueous NH₄F·HF solution effectively removed unreacted SiO₂, but it had to be carefully used to avoid dissolving the generated Si.

For the LiCl-MgCl₂ melt, in which the Mg solubility is higher, the yield of Si was better than in the NaCl-MgCl₂ melt. It is likely that the Mg reducing agent was dissolved in the MSs as a *metal fog* and thus the production of Mg₂Si was suppressed. The yield of Si is expected to increase when molten salts with higher Mg solubility and MgCl₂ salt with higher purity are used.

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