Formation of SiO and Related Si-Based Materials Through Carbothermic Reduction of Silica-Containing Slag

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Silicon based nanoparticulates of various composition and morphology have been produced by smelting reduction method which includes a carbothermic reduction of $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO}$ starting materials to SiO vapor at 2073 K and transfer of the vapor with a carrier-gas to cooler surfaces inside the experimental reactor where the nanoparticulates were deposited. The chemical composition of the starting materials was matched to the basic composition of silica-rich coal ash which is considered as a potential source of Si in this study. Special emphasis was placed upon examining the degree of SiO_2 reduction from starting materials, purity and morphology of the as-obtained nanomaterials. It is shown that up to 20% of Si can be converted from the silica-based melt into rounded nanoparticles, nanoparticle chains and nanowires containing Si, O and C in variable proportions depending on deposition temperature and gas flow conditions. The diameter of nanoparticulates was estimated to be in the range of 20~100 nm. The nanoparticles and chains were found to be deposited at lower temperature locations (293~1320 K) while the nanowires were obtained at higher temperatures (1320~1570 K). There was a tendency for an increase in Si concentration in order of nanowires, nanoparticles chains and nanoparticles. The carbon concentration, on the contrary, was much higher in nanowires as compared to that in nanoparticles. Although the degree of SiO_2 reduction from silica-containing melt to SiO vapor is limited because a part of SiO_2 reacts with C producing SiC, its good controllability, high productivity and possibility for processing cheap starting materials make the smelting reduction a very attractive technique for production of silicon based nanostructured materials.

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1. Introduction

Owing to their unique properties, silicon and its compounds continue to play an important role in designing semiconductor and optoelectronic devices. Over the last years, increasing demands for miniaturization of electronic systems have become a key driver of developing advanced micro- and nanostructured Si-based materials as well as methods for their production. Recently, several routes for synthesis of Si-based nanowires, nanospheres, nanoagglomerates have been experimentally verified including thermal evaporation and laser ablation. The synthesis principle is based on the ability of Si to form a volatile monoxide SiO in the presence of oxygen in the system. In the experiments, commercially available SiO ,^{1,2)} SiO_2 ³⁾ or a Si-SiO₂ mixture^{4,5)} was heated up in an inert gas atmosphere under a lower pressure. This resulted in formation of SiO vapor and its following condensation on cooler parts of the experimental reactors where the SiO vapor was transferred by the inert carrier gas. The experiments showed that temperature is the process key parameter in controlling both the SiO evaporation rate and morphology of nanostructured particles condensed. Although the temperature of heating sample was varied depending on material system used, 1600°C for SiO_2 , 1400°C for Si-SiO₂ mixture and 1100°C for SiO, the tendency for increasing the yield of nanostructured product with temperature was similar for all these studies. Besides, the yield of Si nanowires was found to increase with increasing pressure of Ar carrier gas.¹⁾ However, because the working temperatures of the above methods are comparatively low, they are very limited in quantity of synthesized Si-based nanomaterials.

Constantly increasing demands for the nanometersized Si-based materials will cause the need for production of the Si-

based nanomaterials in a larger amount. The above findings suggest that one of the processes, which could meet this need is smelting reduction. This process is one of the commonly used techniques in pyrometallurgy for reductive refining of oxide-based materials. The process involves supplying energy to melt starting materials in an appropriate reactor and performing relevant chemical reactions in the molten bath under controlled conditions such as gas atmosphere, temperature and pressure inside the reactor. Because the process is performed at very high temperatures, it offers better productivity as compared with other processes.

The concept of such a process has been reported by one of the authors of the present study.⁶⁾ Although the proposed two-stage reduction process was aimed at producing silicon, it has been shown that a vigorous formation of SiO vapor can be achieved by reducing pure molten silica by solid silicon carbide at a temperature of 2073 K and higher under a lower pressure in the system. Based on the proposed concept, we undertook the present study to examine experimentally the applicability of the smelting reduction processes for synthesis of micro- and nanostructured silicon based materials. The synthesis principle is based on the following three steps: carbothermic reduction of silica-containing slag to SiO vapor, transport of the vapor by a carrier gas, and condensation of SiO from the vapor at cooler parts of reaction chamber. Depending on temperature and gas phase composition, after condensation SiO can undergo further chemical reactions producing silicon, silicon suboxide or silicon carbide. A premelted slag composed of SiO_2 , Al_2O_3 and CaO in a molar ratio of 1.0/0.17/0.15, was used as a starting material. This ratio corresponds to that of the basic components in silica-rich coal ash which is considered as a potentially usable source of Si in the present study. Such a coal ash is generated in huge quantity as a by-product during

combustion of some kinds of higher-rank coals.

In the present study, we examined effects of gas flow and temperature inside the reaction chamber on the degree of SiO_2 reduction from silica-containing melt, on purity and morphology of the as-obtained product. For a better understanding of the mechanism of the chemical reactions involved in the process, composition of exhaust gas and slag residue were also investigated. Chemical analysis was performed by an electron probe microanalyser (EPMA) with an energy and wave dispersive X-ray spectrometers. Phase composition of slag residue was investigated by X-Ray diffraction (XRD) method. Size and shape of the obtained nanomaterials were observed with a scanning electron microscope (SEM). More comprehensively, characteristics of the synthesized nanomaterials will be discussed in our next paper.

2. Experimental Setup and Procedure

Figure 1 is a schematical representation of experimental apparatus. A crucible (I.D. 0.04 m, height 0.17 m), made of graphite (density $1850 \text{ kg}\cdot\text{m}^{-3}$, total impurity $<500 \text{ ppm}$) was put inside a sealed water-cooled reaction chamber made of quartz. The chamber was installed coaxially with an induction coil powered by a 15 kW, 100 kHz generator. The experiments were performed under an atmosphere of highly purified Ar gas introduced into the chamber through an inlet tube at a certain flow rate under a pressure close to atmospheric one. The graphite crucible was covered by a graphite threaded lid with three holes, one of which was drilled at the lid center and the others were close to the lid edge. The latter two holes served to let Ar gas flow into the graphite crucible from the inner space of the chamber. Ar gas flow over the crucible and then entered an outlet graphite tube (I.D. 0.01 m) fixed at the lid center hole so that the lower end of tube was separated from the crucible bottom by a certain distance, h . The upper end of the tube was jointed with an outlet alumina tube of the same diameters which, in turn, was connected to a holder of a glass fiber filter. In some experiments a different type of the graphite tube was used. The tube consisted of a graphite outer tube (I.D. 12 mm) and 12 graphite rings (I.D. and height 10 mm) enclosed in the outer tube (not shown here).

During an experiment run, exhaust gas, leaving the

graphite crucible, was analyzed for CO and CO_2 continuously by an IR-analyzer after passing through a fine filter. The flow rate of the exhaust gas was measured by means of a wet flow meter. All the measurement data were stored by a PC.

The slag, or model coal ash, was prepared as follows. Predetermined amounts of reagent grade of $\alpha\text{-Al}_2\text{O}_3$, SiO_2 (quartz) and CaO (calcined from CaCO_3) were mixed and melted in the induction furnace at a temperature of about 1873 K. The slag was fully glassy and no segregation nor deposited phase was observed. The slag contained SiO_2 (68.64 mass%), Al_2O_3 (22.62 mass%) and CaO (8.75 mass%) as verified by EPMA analysis. The slag was crushed and mixed with a pure powdered carbon in a molar ratio of 0.7 relative to amount of SiO_2 in the slag. This ratio was chosen from assumption that the remainder of carbon should come from the graphite crucible. Then, the slag-carbon mixture was pelletized with a 8-mm diameter die. A very small amount of aqueous starch solution was added as a binder. The pellets were dried at 105°C for 24 h to remove the remaining moisture.

The experimental procedure was as follows. The graphite crucible was heated to the desired temperature under an atmosphere of Ar of the constant flow rate ranged within $2.5\sim 33.3 \times 10^{-6} \text{ Nm}^3\cdot\text{s}^{-1}$. The temperature was measured by a W/Re- thermocouple (W-5%Re vs. W-26%Re), which was inset inside the graphite crucible through the graphite and alumina tubes from the top. The tip of the thermocouple was placed at a distance of 0.01 m above the crucible bottom. In the present study, all experiments were made at 2073 K. After the temperature reached this temperature, a few pellets (total mass about 5~6 g) were loaded into the crucible. This moment was considered as starting time of the experiment. Each experiment was continued typically for 30 min. After experiment, the reaction chamber was cooled down to room temperature under Ar atmosphere.

In the present study, particular emphasis has been placed on the chemical composition of the as-obtained product. The concentration of Si, Al, Ca, C and O was measured by means of EPMA (JEL JXA-8200) equipped with the energy dispersive X-ray (EDX) and wave length dispersive X-ray (WDX) analysis. The same techniques were used also to investigate the element distribution over crucible residues. The measurements were performed at a beam accelerating voltage of 15 kV and current of 30 nA under a take-off angle of 38° .

XRD technique (Rigaku, RINT 2200) was used to detect the crystalline phases presented in the crucible residues. The XRD patterns were taken with $\text{CuK}\alpha$ radiation over the range of 10 to 80° at a speed of $0.05^\circ \text{ s}^{-1}$. The crucible residues were also examined by a digital microscope for the observation of the constitution of the residues after experiment. For this purpose, sections were cut out from residue containing crucible parts and were polished with $1 \mu\text{m}$ diamond powder.

A scanning electronic microscope (SEM, Hitachi, S-4100L) was applied to examine the particle size and surface morphology of the materials yielded in the experiments. The SEM micrographs were taken at an accelerating voltage of 15 kV and working distance of 5~15 mm.

Fig. 1 Experimental setup.

3. Experimental Results and Discussion

3.1 Chemical reactions in the melt

A number of chemical reactions can result in SiO formation under the given experimental conditions. Initially, the molten slag components (SiO_2 , Al_2O_3 and CaO) can react with carbon at the surfaces of carbon particles or graphite crucible wall. These reactions can be termed as primary. To make an estimate of what species would be formed as a results of these reactions, partial pressures of gaseous matters, amounts of liquid and solid matters (if exist) were calculated for corresponding equilibrium states under experimental temperature of 2073 K and pressure of 0.1 MPa by using the thermochemical software and database FactSage with the built-in option of predicting component activities in glassy slag. According to the results, the dominant components of gas phase are CO and SiO. Although the partial pressures of SiO, P_{SiO} , and CO, P_{CO} , were changed with molar ratio of SiO_2 in slag to C in graphite, their sum, $P_{\text{CO}} + P_{\text{SiO}}$ was 0.9999 regardless of the ratio. Another feature of the reacting system is a strong trend towards formation of solid silicon carbide, SiC. Therefore, it is concluded that the system should include gaseous CO and SiO, newly formed solid SiC and the rest of slag.

Thus, based on the above equilibrium concept, one can write the following primary reactions

Then, the reaction products can be involved in other reactions with slag components or carbon which can be termed as secondary. Analysis of the available literature (for example⁷⁾) showed that at least two secondary reactions are of prime importance for the following discussion

Since reactions (1) and (3) produce SiO, their proceeding is favorable for the transfer of Si from slag to gas phase. On the other hand, formation of SiC according to the reactions (2) and (4) is unfavored for the process because the SiC formation occurs with consumption of SiO_2 or SiO.

3.2 Location of silicon suboxide deposition

It was observed in the experiments that the slag-C pellets were melted down for a few seconds after loading. Immediately afterwards, as a result of reactions between the melt and carbon, a vigorous evolution of gaseous CO and SiO started. The gas mixture was diluted with Ar carrier gas, which flowed over the crucible. Then, Ar-CO-SiO gas was transferred into the graphite and alumina tubes. As the gas mixture passed inside the tubes, SiO was condensed and deposited as silicon suboxide, SiO_x on the surfaces of cooler parts inside the tubes while Ar-CO mixture arrived at the gas analyzer and wet gas meter.

The deposit was collected at three locations: 1—the inner wall of crucible and the outer surfaces of graphite tube, 2—the inner surfaces of graphite and alumina tubes, and 3—the filter. The deposit amount was dependent on the gas flow conditions. In the present experiments, the gas flow con-

Fig. 2 Appearance of deposit on crucible wall under different flow conditions of carrier gas.

ditions were controlled by two experimental variables: the flow rate of Ar carrier gas, V_{cg} , and the distance between graphite tube tip and crucible bottom, h . At larger h or/and smaller V_{cg} , the deposition occurred mostly on the wall inside the crucible and outer surface of graphite tube. These conditions are undesirable for the process because they make the deposit growth hardly controllable. On the other hand, higher V_{cg} and smaller h were more favorable for collecting the deposit on the inner surfaces of graphite and alumina tubes as well as on the filter due to a fast carrying of SiO vapor from high temperature zone. Under these conditions, the first portion of brown-colored deposit was already observed on the filter within a minute after the pellets were loaded. However, the largest amount of deposit was collected inside the tubes. The distance h appears to be more important parameter for the control of deposition location than V_{cg} . When h exceeded 0.08~0.1 m, a significant amount of deposit was collected on the crucible wall even at higher flow rates of Ar carrier gas.

Figure 2(a,b) shows appearance of deposit on crucible wall under different flow conditions of carrier gas: $V_{\text{cg}} = 3.11 \times 10^{-5} \text{ Nm}^3 \cdot \text{s}^{-1}$ and $h = 0.185 \text{ m}$ (a), and $V_{\text{cg}} = 1.21 \times 10^{-5} \text{ Nm}^3 \cdot \text{s}^{-1}$ and $h = 0.04 \text{ m}$ (b). In Fig. 2(a), the crucible inner wall is copiously covered by a white deposit growing from the wall surface to the crucible center. This resulted in a formation of fibre-shaped fragments inside the crucible as shown in the figure. However, when h was as smaller as 0.04 m, as seen in Fig. 2(b), there is no deposit on the surface of crucible.

3.3 The degree of SiO_2 reduction and product purity

Figure 3 shows relative mass of deposit inside the tubes and on filter, M_d , as a function of flow rate of carrier gas, V_{cg} , at a constant $h = 0.04 \sim 0.045 \text{ m}$. The value M_d was defined as the ratio of the mass increment of tubes during experiment to the mass of SiO_2 in loaded pellets. As seen in the figure, higher gas flow rate gives larger M_d , that results from the increase in mass transfer rate of SiO from the melt surface. A visual examination of the tubes after experiments revealed that their inner walls were completely covered with the differently colored deposit except some parts very close to the graphite tube lower tip. The color, although not shown here, was varied from light gray at lower places inside the graphite tube to brown at upper places inside the graphite and alumina tubes, and at the filter. Especially large amount of deposit was obtained at the places distanced from the lower

Fig. 3 Effect of carrier gas flow rate on relative weight of deposit.

Fig. 4 Variation of SiO_2 reduction degree (a) and contamination level (b) with temperature.

tip of graphite tube by 0.04~0.06 m. This led to clogging of the tube with the deposit during experiments.

In a few experiments several graphite rings were placed inside graphite tube. The deposit mass was determined at each ring wall from the mass changes of each rings after experiments. The composition of deposit was measured by EPMA also at each ring position. Figure 4(a) presents a typical variation of the degree of SiO_2 reduction from slag, $M_{\text{Si,d}}/M_{\text{Si,s}}$, with temperature inside the graphite tube. Here, $M_{\text{Si,d}}$ and $M_{\text{Si,s}}$ are the masses of Si in deposit collected by an appropriate ring and that in starting sample, respectively. The results were obtained under $V_{\text{cg}} = 1.77 \times 10^{-5} \text{ Nm}^3 \cdot \text{s}^{-1}$ and $h = 0.04 \text{ m}$. In the figure, the highest temperature corresponds to the tube lower tip while the lowest one pertains to an upper location inside the tube distanced from its lower tip

by about 0.13 m. The temperature inside the tube was determined from prior measurements.

As seen from Fig. 4(a), there is a temperature zone between 1440~1700 K within which the most amount of deposit was collected. In this zone about 20% of total deposit condensed. Concentration of metal impurities, such as Al and Ca, in the deposit was strongly dependent on local temperature inside the graphite tube. Figure 4(b) shows contamination level of the as-obtained deposit with temperature inside the graphite tube. The data were obtained under the same experimental conditions as those in Fig. 4(a). The contamination level is defined as the ratio between total mass of impurities, $M_{\text{imp,d}}$, and Si, $M_{\text{Si,d}}$, in the deposit. As seen in the figure, the deposit is contaminated with metal impurities at temperatures higher than 1600 K. The metal impurities are indicated at the bars in order of decreasing their concentration from the top. The main impurities are Al and Ca entering the deposit possibly through the gas phase as relatively volatile aluminum suboxide, Al_2O and calcium vapor. Thermodynamic estimations showed that, in the systems $\text{Al}_2\text{O}_3\text{--C}$ and CaO--C , the vapor pressures of Al_2O and Ca are much higher than those of other species containing Al and Ca, respectively. For example, on the basis of thermodynamic data, at $T = 2073 \text{ K}$ and total pressure equals to unity, partial pressures of Al_2O and Ca, $P_{\text{Al}_2\text{O}}$ and P_{Ca} , are calculated as 9.8×10^{-3} and 6.5×10^{-3} respectively at the equilibrium of $\text{C--Al}_2\text{O}_3$ and C--CaO systems. It is to be noted that these partial pressures can be the maximum estimates at the lower limit of SiO_2 content in the slag.

The lower limit of the temperature, above which the contaminant content is high, shifted to higher values as V_{cg} decreased. For example, it was about 1700 K at $V_{\text{cg}} = 3.4 \times 10^{-6} \text{ Nm}^3 \cdot \text{s}^{-1}$ and $h = 0.04 \text{ m}$. Below the lower limit temperature, the content of metal impurities was very low according to the results of EPMA analysis.

The collected deposit was analyzed for Si, O and C compositions by EPMA/WDX technique. To be able to measure the carbon concentration, the samples were coated with Al instead of C which is commonly used for sample coating. Figure 5 presents the temperature dependence of Si, O and C concentrations in the deposit collected at locations of very low level of Al and Ca impurities except for two dots at $T > 1600 \text{ K}$. In the figure, each value was obtained by averaging the results of 4~5 measurements. As seen from this figure, carbon concentration becomes significantly lower as the deposition temperature decreases. The silicon concentration, on the contrary, is slightly increased with the decrease in temperature. The deposit on the filter contains about 54 mol% of O and 45 mol% of Si while the carbon concentration is less than 1 mol%. In this case, molar ratio of O to Si is 1.2 indicating that the deposit composition is close to silicon monoxide.

3.4 Deposit morphology

Results of SEM analysis showed that the deposit presents nanostructured material of three types with different morphologies: nanoparticles, nanoparticle chain and nanowires depending on location where the deposit was collected. The deposit contained also comparatively large spherical particles

Fig. 5 Variation in Si, O and C concentration with temperature.

with size ranging from 100 to 1000 nm. However, they were not typical under the present experimental conditions and were observed in a small quantity only at larger gas flow rates.

Figure 6 presents SEM views of deposit grown on the inner surfaces of graphite tube under the same conditions as those for the data shown in Fig. 4: flow rate of carrier-gas, $V_{cg} = 1.77 \times 10^{-5} \text{ Nm}^3 \cdot \text{s}^{-1}$, and tube position, $h = 0.04 \text{ m}$. The nanoparticles (Fig. 6(a)) were found only at lower

temperatures of $T < 920 \text{ K}$. Their size was estimated as 40~60 nm. The deposit on the filter also consisted of nanoparticles of the same size and morphology. Nanowires were dominated at higher temperatures. Figure 6(c) shows nanowires grown at 1490~1580 K where the largest amount of deposit was obtained. In the intermediate temperature range, the deposit consisted mainly of straight or slightly curved nanoparticle chains of variable length as exemplified in Fig. 6(b) for 1220~1320 K.

It was found that carrier gas flow rate, V_{cg} , and tube position, h , are of prime importance in controlling the size and morphology of the nanostructures. At smaller h , (0.04~0.045 m), the size of nanoparticles increased with decreasing carrier gas flow rate, V_{cg} . However, when V_{cg} became smaller than $3.4 \times 10^{-6} \text{ Nm}^3 \cdot \text{s}^{-1}$, no single particles were observed inside the reaction chamber because the particles formed chains. The similar result was obtained at larger h , ($>0.07 \text{ m}$) even at larger V_{cg} . When h was larger than 0.145 m, only nanowires of 30~50 nm in diameter were observed on the filter and surfaces inside the tubes.

There was a tendency for the nanowire length to increase with h . When the deposit was grown on the crucible walls, it consisted of long and smooth nanowires regardless of gas flow condition. An example of the wires are presented in Fig. 6(d). It is noteworthy that the deposit color was changed from brown through light yellow to light gray as the particles turned into the chains and nanowires.

3.5 The process kinetics and mechanism

As readily seen from the previous section, the most reactions involved occur with CO formation. Information on

Fig. 6 SEM views of as-obtained deposit at different temperatures inside tube: a) $<920 \text{ K}$, b) 1220~1320 K c) 1490~1580 K, and d) on crucible wall.

Fig. 7 Change in CO gas outflow rate with time.

CO evolution rate would be helpful for an understanding of kinetic aspects of the reaction system. The rate was determined from measurements of CO concentration in exhaust gas and gas volume as explained above. Figure 7 presents time variations in the rate of CO gas, V_{CO} , leaving the crucible under various experimental conditions. Inasmuch as the CO outflow rate was inherently dependent on the total weight of pellets, V_{CO} was expressed in a dimensionless form as molar rate of CO divided by molar quantity of SiO_2 in the initial oxide-carbon mixture. The time dependence of V_{CO} can be subdivided into three periods as indicated by corresponding figures and broken lines in Fig. 7. During the first period, the CO rate increased up to a maximum value, whereupon abruptly decreased for a time not longer than 5 min. Then, the rate was kept constant with time during the second period. Duration of the second period was about 10 min. The last third period was characterized by the further decrease in V_{CO} . Such a variation in CO outflow rate suggests that conditions for reactions to proceed in the given system are changed with time.

To gain more detailed information about the reaction mechanism, a series of experiments was conducted under the same conditions except the reaction time. The conditions were $V_{cg} = 1.27 \times 10^{-5} \sim 1.65 \times 10^{-5} \text{ Nm}^3 \cdot \text{s}^{-1}$, $h = 0.04 \text{ m}$ and $T = 2073 \text{ K}$. In two experiments, the reaction was stopped at 5 and 10 min, respectively, with a rapid cooling down of the reaction system by the cut of the heater power supply. In the third experiment, the reaction time was 30 min that was the standard duration in the present study. After experiments, the crucibles were cut lengthwise to make sections containing residue in the crucible. Then, the residue was characterized by XRD and EPMA and, additionally, the residue constitution was examined with an optical microscope.

Figure 8 shows the XRD patterns of residual materials for all the three experiments. Two tendencies can be clearly seen in this figure. The first is the SiC formation beginning at the very early stage of the reduction process. This is confirmed by a few peaks of relatively low intensity of SiC observed

Fig. 8 XRD patterns of as-quenched residue in crucible.

already at the XRD for the experiment of 5 min. The second tendency is a rapid decrease in amount of glassy phase in the slag melt with the reaction time. In the case of 5 min, a broad background in the XRD pattern indicates the presence of amorphous glassy phase in significant amount. At 10 min, on the other hand, according to the XRD pattern, the amount of the glassy phase is very small. It should be noted that we could not identify exactly some peaks in the XRD patterns which correspond supposedly to complex crystalline oxides of Al-Ca-Si system. Some possible compositions are indicated in the figure.

The similar tendencies can be observed in the digital microscope photographs of the cross-section of the as-quenched residues as shown in Fig. 9. Each photograph presents typical images for 5, 10 and 30 min, respectively. At 5 min, the residue presents glassy layer observed as black background in Fig. 9 containing a lot of fine particles viewed as white dots in the figure. To verify the particle composition, the cross-section of the residue was selectively analyzed for the contents of Si, Al and Ca by EDX. According to the analysis results, the particles of $3 \sim 5 \mu\text{m}$ in size were enriched with Si, and conversely were depleted with Al and Ca as compared to the composition of the glass matrix. Calculations showed that chemical composition of the particles was very close to that of SiC. Hence, the fine white particles in Fig. 9(a) are most likely to be SiC inclusions. At 10 min, quantity of SiC inclusions increased significantly, and their shape became more acicular. At 30 min, the residue was abundant of SiC which looks gray colored clusters consisting of very fine inclusions in Fig. 9(c). At this reaction time, EPMA results revealed that minor volume of glassy phase

Fig. 9 Appearance of slag residue in crucible after experiment.

contain about 5 mass% of SiO_2 , 31 mass% of CaO and 64 mass% of Al_2O_3 .

Thus, the three periods of the process in Fig. 7 can be explained as follows. At the very first stage, the vigorous emission of CO occurs because SiO_2 of the melt reacts directly with carbon on the still-fresh surfaces of graphite particles or crucible according to reactions (1) and (2). This results in converting the carbon surfaces to SiC . Since the SiC layer offers resistance to diffusion of C and Si at the solid side interface, mass transfer of the reaction reagents through the layer starts to play an increasingly important role in controlling the overall reaction rate. As a result, the SiO_2 reduction rate and thus CO formation rate are decreased as the SiC layer thickness increases. This decrease can be observed in Fig. 7 during the last stage of the first period. In the second period, the very weak time dependence of CO emission rate can be explained from the assumption that the growing SiC layer can contain pores which could maintain a fast diffusion of gaseous species to the reaction zone. This assumption can be confirmed by the following experimental observations and by the data reported in the relevant literature.⁸⁾

Slag residue and parts of crucible bottom adjacent to the

Fig. 10 A view of transition layer between slag and crucible bottom.

Fig. 11 EDS profiling of slag and transition layers.

slag were investigated by EPMA. The results indicated existence of a transition layer between the slag residue and graphite of the crucible. At the center of crucible bottom, the layer thickness was 250~300 μm at 5 min and 400~500 μm at 10 min. Figure 10 shows a SEM view of a part of transition layer at 10 min. To examine the in-depth distribution of the layer components, EDX profiling was performed for Si , Al and Ca . Figure 11 shows the profiling results. Slag residue region (A–B, Fig. 10), except a small area around point A is rich in Al and Ca and poor in Si . On the other hand, the transition layer (region below B) is enriched with Si and carbon while concentrations of Al and Ca are much less. Here, higher concentrations of Si at the peaks suggest that it exists in the transition layer in the form of SiC . This was confirmed also by additional EPMA/WDX measurements.

The zones of the transition layer between the SiC peaks were found to be composed of carbon. In the Fig. 10, these zones look as black spots.

These observations imply that the reaction of SiC formation can proceed in the bulk of crucible bottom. This is supported by the data on reaction mechanism between SiO₂ and graphite available in the literature. Paccaud and Derre⁸⁾ reported that, on heating a SiO₂–SiC powder mixture with a carbon piece up to temperatures of 1673~1973 K, formation of SiC on the carbon surface occurred due to gaseous diffusion of SiO onto fresh carbon surface through connected pores in the carbon piece. These pores are grown intrinsically since the SiC formation causes stress due to a difference in density between C and SiC. The stress originates the generation and propagation of cracks inside the bulk of graphite. Then, a newly generated fresh surface of graphite is exposed to gaseous SiO resulting in formation of new portions of SiC. Therefore, keeping the rate of CO emission during the second period of the reduction process (Fig. 7) can be explained by a recurring renewal of surface for the reaction between SiO and C inside the carbon particles or graphite crucible parts. The further decrease in reduction rate during the third period at Fig. 7 is probably associated with a significant diminish of SiO₂ amount in the system due to its consumption for the reactions.

4. Conclusions

The experimental verification of the smelting reduction process showed that nanosized silicon based materials can be synthesized by carbothermic reduction of silica containing starting materials containing alumina and calcia. In the present study, the chemical composition of the starting materials was matched to the basic composition of silica-rich coal ash which is considered as a potentially usable source of Si. The main point of the process is melting the starting materials at 2073 K, reducing SiO₂ to SiO vapor and carrying the vapor with Ar-CO carrier gas mixture through a graphite tube from the highest temperature zone (above melt surface) to cooler parts of experimental reactor (filter and inner surfaces of the tube) where the vapor is condensed as SiO_x followed by further chemical transformations.

It is found that the degree of SiO₂ reduction from slag, purity and morphology of the as-obtained nanoparticulates were governed by temperature and carrier-gas flow conditions. Higher flow rates of carrier gas and shorter distances between the graphite tube lower tip and melt surface were favor for SiO₂ reduction. In these conditions, about 20 mass% of Si, contained initially in the molten slag as SiO₂, was converted into Si in the form of nanostructured Si-based material which was deposited on the inner tube surfaces and filter. Elemental analysis showed that the material consists of Si, O and C with atomic fractions varying

with the deposition temperature. As the temperature became lower, concentration of C is decreased while that of Si is slightly increased.

Depending on temperature, the material presented chiefly rounded nanoparticles (<920 K), nanoparticle chains (920~1320 K) or nanowires (1320~1570 K). The nanoparticulate diameter was ranged from 20 to 100 nm with a trend toward a decrease as the gas flow rate increases. The nanoparticles and nanochains were free of metal impurities while the purity of nanowires was dependent on deposition temperature. If the temperature exceeded a threshold value, the deposit was highly contaminated with metal impurities such as Al, Ca, K and Fe. Under the present experimental conditions, the threshold value was ranged from 1600 to 1700 K depending on carrier gas flow rate. At lower carrier-gas flow rate and/or larger tube distance, nanoparticles were transformed into the nanoparticle chains, which, in turn, were changed into the nanowires on further decreasing the carrier-gas flow rate and/or increasing the tube distance. However, the decrease in carrier-gas flow rate and/or increase in tube distance led to a significant drop in the degree of SiO₂ reduction.

It is shown that the limitations in the efficiency of SiO₂ reduction are associated with a strong tendency of C to react with SiO₂ or SiO producing SiC in the present reaction system. About 50% of Si was converted into SiC under the given experimental conditions. Nevertheless, it is believed that the smelting reduction process is a promising candidate for potential application in the production of Si-based nanostructured materials due to its good controllability, high productivity and possibility for processing cheap and plentiful silica-containing materials.

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