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Abstract

The reduction of quartz was studied isothermally in a fluidized bed reactor using continuously flowing methane-hydrogen gas mixture in the temperature range from 1623 K to 1773 K (1350 °C to 1500 °C). The CO content in the off-gas was measured online using an infrared gas analyzer. The main phases of the reduced samples identified by XRD analysis were quartz and cristobalite. Significant weight loss in the reduction process indicated that the reduction products were SiO and CO. Reduction of SiO₂ to SiO by methane starts with adsorption and dissociation of CH₄ on the silica surface. The high carbon activity in the CH₄-H₂ gas mixture provided a strongly reducing condition. At 1623 K (1350 °C), the reduction was very slow. The rate and extent of reduction increased with the increasing temperature to 1723 K (1450 °C). A further increase in temperature to 1773 K (1500 °C) resulted in a decrease in the rate and extent of reduction. An increase in the gas flow rate from 0.4 to 0.8 NL/min and an increase in the methane content in the CH₄-H₂ gas mixture from 0 to 5 vol pct facilitated the reduction. Methane content in the gas mixture should be maintained at less than 5 vol pct in order to suppress methane cracking.

Keywords

mixtures, quartz, monoxide, reduction, methane, hydrogen, silicon

Disciplines

Engineering | Science and Technology Studies

Publication Details

Li, X., Zhang, G., Tronstad, R. & Ostrovski, O. (2016). Reduction of quartz to silicon monoxide by methane-hydrogen mixtures. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science*, 478 2197-2204.

Reduction of Quartz to Silicon Monoxide by Methane–hydrogen Mixtures

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Abstract

The reduction of quartz was studied isothermally in a fluidized bed reactor with continuously flowing methane–hydrogen gas mixture in the temperature range of 1623 K (1350 °C) to 1773 K (1500 °C). The CO content in the off-gas was measured online using an infrared gas analyzer. The main phases of the reduced samples identified by XRD analysis were quartz and cristobalite. Significant weight loss in the reduction process indicated that the reduction products were SiO and CO. Reduction of SiO₂ to SiO by methane starts with adsorption and dissociation of CH₄ on the silica surface. The high carbon activity in the CH₄–H₂ gas mixture provided a strongly reducing condition. At 1623 K (1350 °C), the reduction was very slow. The rate and extent of reduction increased with increasing temperature to 1723 K (1450 °C). A further increase in temperature to 1773 K (1500 °C) resulted in a decrease in the rate and

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1 extent of reduction. An increase in the gas flow rate from 0.4 to 0.8 NL/min and increase in
2 the methane content in the CH₄-H₂ gas mixture from 0 to 5 vol pct favored the reduction.
3 Methane content in the gas mixture should be maintained below 5 vol pct in order to suppress
4 methane cracking.

5 **I. Introduction**

6 Metallurgical silicon and ferrosilicon alloys are produced in submerged electric arc furnaces
7 by carbothermal reduction of silicon bearing oxides (typically quartz) with carbonaceous
8 materials. Coal, coke, charcoal and woodchips are commonly used as reductants in these
9 processes [1]. Carbothermal reduction requires high temperatures and is energy intensive.
10 The contents of trace elements in both quartz and reductants determine the purity of the
11 produced silicon [2]. SiC is also produced by the carbothermal reduction of quartz.

12
13 Silicon monoxide (SiO) vapor is one of the major intermediate species in the production of
14 SiC and metallurgical silicon [3, 4]. SiO₂ is reduced by carbon to SiO by the following
15 reaction:

18
19 SiO further reacts with carbon to form SiC:

The primary reaction for production of Si is the following:

Methane has the advantage of high purity over conventional carbonaceous reductants such as coal or coke which always contain impurities [5–7]. The gas-phase reaction between SiO and methane with or without a catalyst has been used for synthesis of SiC whiskers [8–12]. However, no reports were found in the literature on the direct reduction of SiO₂ to SiO by the methane-containing gas. The purpose of the present study is to investigate the possibility of reduction of quartz to SiO via the gas–solid reaction by methane–hydrogen gas mixture, as described by Reaction [4]. Natural gas contains low harmful impurities of solar silicon, and provides high carbon activity for the reduction of quartz, which makes it an attractive reductant over conventional solid carbon.

Above 1729 K (1456 °C), Reaction [4] has a negative Gibbs free energy change under standard conditions (ΔG°); at 1873 K (1600 °C), $\Delta G^\circ = -63.2$ kJ (calculated using HSC Chemistry 6.1). However, methane is unstable at temperatures above 823 K (550 °C); it cracks with deposition of solid carbon (Reaction [5]) at temperatures above 1273 K (1000 °C) [13]. Solid carbon deposits on the sample surface, hindering further progress of the reduction

by blocking the quartz particle surface.

Therefore, reduction of metal oxides by the methane-containing gas should be conducted under conditions at which cracking of methane is limited.

This study examines the effects of temperature, gas composition and gas flow rate on the reduction of quartz in the fluidized bed reactor by the CH₄–H₂ gas mixture with a low CH₄/H₂ ratio to suppress methane cracking. Reduction of quartz to SiO can be of commercial interest; however, scaling up and further study of this process are needed to find feasibility of the industrial reduction of quartz by the methane-containing gas.

II. Experimental

A fluidized bed reactor was adopted to mitigate the effect of carbon deposition on the surface of quartz particles. Quartz powder with a particle size of 100–140 μm was obtained by crushing and grinding quartz lumps (supplied by Elkem AS, Norway) by an agate mill and sieving to the size range. The impurity contents in quartz lumps were provided by the supplier, as shown in Table I. The gases (CH₄, Ar and H₂) used in the investigation were of 99.999 pct purity, supplied by Coregas Pty Ltd, Australia.

(Table I)

1 The fluidization of quartz particles was first verified using a cold model of the fluidization
2 reactor made of Perspex material. It consisted of two zones, a fluidization zone (inner
3 diameter 20 mm) in which a fluidized bed was formed, and a settling zone (inner diameter 40
4 mm). The settling zone had an enlarged intersection and therefore a lower gas flow rate,
5 which allowed the quartz particles brought into the settling zone by ascending gas stream to
6 settle and return to the fluidized bed. A connector with a filter was installed at the bottom of
7 the fluidized bed which played a role of a gas distributor. Fluidisation of quartz powder with
8 particle size in the ranges of 53–100 μm , 100–140 μm and 140–200 μm in the cold model
9 was examined using nitrogen with different flow rates. The change of quartz bed was
10 recorded by a video camera (D5100, Nikon Corporation, Tokyo, Japan).

11
12 The schematic of the fluidized bed high-temperature reactor for the reduction experiments is
13 presented in Figure 1. The reactor was made from graphite; it was installed within an alumina
14 tube of 50 mm ID. The inner diameter of the fluidization zone was 20 mm, and settling zone
15 was 40 mm. A type B thermocouple protected by an alumina sheath was inserted into the
16 fluidization zone to measure the temperature before introducing quartz powder, then it was
17 removed from the fluidization zone to avoid disturbing the fluidization of quartz powder
18 during reaction. An alumina tube was inserted into the settling zone which was used to feed
19 quartz samples into the reactor.

20
21 In an experiment, the reactor system was first assembled, purged with argon, and heated to
22 the experimental temperature. Then the methane–hydrogen gas mixture was introduced, and 2

g of quartz was added into the fluidizing zone of the reactor via the feeding tube. After reduction for certain time, the furnace was cooled, the reactor was disassembled, and the sample taken for characterization. Argon was introduced between the graphite reactor and outside alumina tube to make sure that all of the gaseous reacting products were purged out of the reaction system. The total inlet gas flow rate (reducing and purging) was maintained at 1.00 NL/min.

(Figure 1)

The reaction between methane and quartz was also studied using a fused quartz sphere with diameter of 15.90 mm (99.99 pct SiO₂, provided by Guolun Quartz Products Co. Ltd, China) hung in the methane–hydrogen gas mixture. The reaction system was setup in a graphite tube furnace (Model 1000-2560-FP20, GT Advanced Technologies, Santa Rosa, U.S.A.). A quartz sphere was suspended by a tungsten wire with 0.5 mm diameter from the top into the hot zone of a reactor tube (high-purity graphite) with 26 mm internal diameter. A methane–hydrogen gas mixture flowed downward through the tube. The furnace was heated to the targeted temperature at 20 K/min under argon atmosphere. Then the gas was switched to a methane–hydrogen mixture. Reaction was stopped after certain time by lowering the temperature at 20 K/min. After reaction, the sphere was weighed and analyzed.

In both reduction experiments, the off gas composition was continuously monitored and recorded every 5 seconds by an infrared CO/CO₂/CH₄ analyzer (Advanced optima AO2020, ABB, Ladenburg, Germany) connected with a computer.

The original quartz particles and reduced samples were analyzed by X-ray diffraction (XRD, MMA, GBC Scientific Equipment, Braeside, Australia). The fine powder of a sample was scanned at a speed of 0.02 °/s and step size 0.02 ° with CuK radiation generated at 35 kV and 28.6 mA.

SEM images were recorded by field-emission scanning electron microscopy (FESEM, JSM-6000, JEOL, Tokyo, Japan) operated at 15 kV. The chemical composition of the samples was analysed by an energy-dispersive X-ray spectrometer (EDS). The samples were coated with gold to enhance conductivity in SEM/EDS analyses.

The extent of reduction was defined as a fraction of oxygen in quartz removed in the course of reduction, in the form of CO and SiO according to Reaction [4]. Using the CO concentration in the off gas, the extent of reduction (X, pct) was calculated using Eq. [6].

$$X = \frac{2}{n_{O-i}} \int_0^t \frac{F}{22.4} C_{V-CO} dt \quad [6]$$

where C_{V-CO} is the concentration of CO, vol pct; n_{O-i} is the initial content of oxygen in quartz, mol, F is the inlet gas flow rate, NL/min, t is reaction time, min.

III. Experimental Results

A. Cold model of a fluidized bed reactor

The minimum fluidization velocity (U_{mf} , m/s) and terminal velocity (U_t , m/s) of particles

were estimated using the following correlations [14]:

$$U_{mf} = [d_p^2 g (\rho_p - \rho_g)] / (1650 \mu) \quad [7]$$

$$U_t = [d_p^2 g (\rho_p - \rho_g)] / (18 \mu) \quad [8]$$

where d_p = diameter of quartz particles, cm;

ρ_p = density of quartz, g/cm³;

ρ_g = density of fluidization gas, g/cm³;

μ = dynamic viscosity of fluidization gas, g/(cm·s).

The fluidization of quartz particles of different particle size ranges was first verified using a cold model fluidization reactor. The N₂ flow rate was changed from 0.1–1.2 NL/min. Table II compares the measured U_{mf} values with calculated using Eq. [7] and gas properties at 293 K (25 °C). Calculated U_t using Eq. [8] is also listed in Table II.

(Table II)

In the case of quartz particles in the size range 53–100 μm, fluidization by gas with tested flow rate 0.1–1.2 NL/min was not observed; channeling took place in the bed. The minimum fluidization velocity for particles 100–140 μm was close to that calculated by Eq. [7]. In the case of 140–200 μm quartz particles, the measured minimum fluidization velocity was significantly smaller than the calculated value. The terminal gas velocity was not reached in both cases in the tested range of gas flow rate.

The calculated parameters of fluidization of quartz particles with size 100–140 μm by pure hydrogen at temperatures 1623 K (1350 °C) to 1773 K (1500 °C) are listed in Table III. Calculated data indicate that fluidization of quartz particles can be operated in a wide range of H_2 gas flow rate (0.036–1.494 NL/min).

(Table III)

B. Reduction of quartz to SiO in the fluidized bed reactor

Table IV summarises experimental conditions and weights of samples before and after reduction. The effect of temperature was studied in the temperature range of 1623 K (1350 °C) to 1773 K (1500 °C) at constant fluidizing gas flow rate of 0.8 NL/min and gas composition of 5 vol pct CH_4 –95 vol pct H_2 . The reduction extent calculated from the off gas composition was always slightly higher than the extent of reduction found from the weight loss. This discrepancy can be attributed to the loss of some fine SiO_2 particles in the fluidized bed generated from the friction/collision among quartz particles. These fine particles were easily carried out of the fluidized bed by the gas stream. It was noticed that the deviation was greater with higher fluidizing gas flow rate and higher temperature. Therefore, the reduction extent calculated from the off gas composition was more reliable in this investigation.

The change of CO concentration in the off gas vs time at different temperatures is shown in Figure 2. Figure 3 presents the XRD spectra of the samples reduced at different temperatures for 120 min.

(Table IV)

(Figures 2 and 3)

At 1623 K (1350 °C), the CO concentration reached 0.078 vol pct in about 5 min after introducing quartz powder, then declined slowly to about 0.024 vol pct at 40 min. After 120 min of reaction, the extent of reduction calculated from the CO concentration in the off-gas was only 4.4 pct; XRD analysis of the sample after reaction detected only quartz. The reduction at this temperature was very slow. Increasing temperature to 1673 K (1400 °C) resulted in a significant increase of the reduction rate; the CO concentration in the off gas reached 0.37 vol pct after 3.2 min reaction. After 120 min reduction, the extent of reduction was 25.0 pct. Further increasing temperature to 1723 K (1450 °C) accelerated the reaction rate, brought about the extent of reduction to 32.0 pct in 120 min. In addition to the quartz peaks, cristobalite peaks were detected in the XRD spectrum of the reduced sample as a result of the transformation of quartz to cristobalite at high temperatures [15]. Stronger cristobalite peaks were observed in the XRD spectrum of the sample reduced at 1773 K (1500 °C). The CO concentration raised quickly to 1.14 vol pct after quartz powder was introduced to the reaction zone, however, it dropped sharply to less than 0.19 vol pct after 10 min reaction.

No SiC was identified by the XRD analysis of the samples reduced at different temperatures, although further reaction of SiO with CH₄ via Reaction [9] is thermodynamically feasible. This means that either no SiC was formed on the surface of quartz particles or the SiC yield was too low to be detected by XRD. Thermodynamic calculation using HSC Chemistry 6.1 showed that Reaction [9] is practically irreversible with the equilibrium constant in the order of 10⁷ to 10⁸ in the considered temperature range. The fact that Reaction [9] did not occur in

the fluidized bed is attributed to the kinetic barrier in the SiC nucleation in the bed.

The effect of fluidizing gas flow rate on the reduction of quartz was examined at 1723 K (1450 °C) in the range 0.4 to 0.8 NL/min with a constant methane concentration of 5 vol pct. Total gas flow through the gas analyzer (fluidizing and purging) was kept constant at 1.0 NL/min. Figure 4 depicts the change of CO concentration in the off gas vs time for different gas flow rates. At a low gas flow rate of 0.4 NL/min, CO concentration reached 0.27 vol pct nearly instantly when the quartz powder was introduced into the reactor. The peak CO concentration increased nearly proportionally with increasing gas flow rate.

(Figure 4)

The effect of methane content in the gas mixture on the reduction of quartz was examined at 2, 5 and 10 vol pct, keeping fluidizing gas flow rate at 0.8 NL/min and temperature at 1723 K (1450 °C). The change of CO concentration vs time in experiments with different methane contents is shown in Figure 5. The CO peak concentration and extent of reduction increased with increasing methane content in the gas mixture from 2 to 5 vol pct. In the experiment with 10 vol pct of methane, the reduction rate was much faster at the beginning of the reaction, however it decreased dramatically, and the final extent of reduction was low (4.6 pct after 120 min). The sample after reduction became black, indicating deposition of solid carbon on the particle surface due to excessive methane decomposition (Reaction [5]) which

retarded the reduction.

(Figure 5)

IV. Discussion

Reduction of solid silica by gaseous hydrogen–methane mixture is a typical gas-solid reaction in which a gaseous reductant diffuses to the gas-solid phase boundary where reactions take place, and the gaseous products diffuse back into the bulk gas. The rate of the whole process is determined by the slowest step in a series of reactions and mass transfer steps.

Quartz reduction by $\text{CH}_4\text{--H}_2$ gas was strongly affected by the reduction temperature (Figure 2). Applying Arrhenius law to the peak rate of reduction at different temperatures, apparent activation energy of 408 kJ/mol was obtained, with a correlation coefficient of 0.94 between the CO peak concentration (which characterises the rate of reduction) and reciprocal of absolute temperature (Figure 6). Such high activation energy is expected for processes with intrinsic reaction kinetics. According to Figure 4, the reaction rate increased with gas flow rate. The increase of the reaction rate with flow rate is an indication of the effect of the external mass transfer. However, the gas flow rate also affected the thermal cracking of methane in the gas phase [16, 17]; the degree of methane cracking increased with increasing residence time which decreased with increasing gas flow rate. The actual methane concentration in the fluidized bed at the gas flow rates 0.4 and 0.6 NL/min was higher than that at 0.8 NL/min, at which the optimum methane content in the gas stream was established within the range of 5 vol pct (Figure 5). Therefore, increase in the gas flow rate decreased the

actual methane content in the reactor with a positive effect on the reaction rate.

(Figure 6)

Reduction of SiO_2 to SiO by methane proceeds through Reaction (4). The reaction starts with adsorption and dissociation of CH_4 on the silica surface $\text{CH}_4 \rightarrow \dots \rightarrow \text{C}_{\text{ad}} + 2\text{H}_2$. Carbon activity in the system is in the range of 15.2–27.1 [18]. Adsorbed highly active carbon forms strong bonds with oxygen atom and then forms CO which is released from the surface to the gas phase. The removal of an oxygen atom from the silica surface increases the energy states of nearby oxygen and silicon; a volatile SiO molecule is formed and released from the surface.

However, the use of pure methane or $\text{CH}_4\text{--H}_2$ gas mixture with high methane concentration leads to cracking of methane and deposition of carbon black which blocks the reaction sites on the surface of quartz. Moreover, deposition of solid carbon decreases thermodynamic activity of carbon in the system. The major role of hydrogen in the $\text{CH}_4\text{--H}_2$ gas mixture is to control carbon activity in the system avoiding excessive methane cracking. Hydrogen can directly reduce silica to SiO by Reaction [10], which proceeds through adsorption of H atoms on the silica surface [19, 20]. Low partial pressure of H_2O needed for Reaction [10] to occur is maintained by Reaction [11]. A combination of these two reactions gives Reaction [4], therefore thermodynamics of the combination of Reactions [10] and [11] is equivalent to the thermodynamics of Reaction [4]. However, Reaction [4] proceeds under strongly non-equilibrium conditions; the use of active carbon secures reduction of SiO_2 to SiO .

Following Reaction [4], methane diffuses to the reaction interface while SiO, CO and H₂ diffuse away from the reaction interface. Mass transfer of SiO and CO in the gas phase can contribute to the reaction rate control. The concentration of hydrogen in the gas phase is quite high; its diffusion is not expected to have an effect on the rate of reaction.

The low degree of conversion of SiO₂ to SiO can be explained by the low specific surface area of quartz sand (estimated value 0.008–0.011 m²/g). Decrease in the rate of reduction with reaction time and relatively low extent of reduction was related to the deposition of carbon black as described above. Moreover, the change in the rate controlling mechanisms in the course of reduction cannot be excluded.

The reduction of quartz was studied further using quartz spheres, which were suspended by a tungsten wire in the CH₄–H₂ gas mixture. The methane content in the gas mixture was maintained at 0.5 vol pct to minimize the effect of the methane cracking. The change of CO concentration vs time in the off gas is presented in Figure 7. The CO concentration decreased rapidly in the first 40 min. With the increase of the reaction temperature, the reaction rate increased, and the CO concentration curve became more fluctuant.

(Figure 7)

Applying Arrhenius law to the apparent reaction rate constant obtained from Figure 7, apparent activation energy was obtained to be 207 kJ/mol. This value is only about 50 pct of the value obtained from experimental data using the fluidized bed reactor, indicating that the reaction rate was affected by the external diffusion of gas species from the reaction interface. Continuous movement of the quartz particles in the fluidized bed reactor generated a stirring effect; the effect of external diffusion on the reaction rate in the fluidized bed reactor was relatively small.

The surfaces of quartz spheres after reduction at 1723 K (1450 °C) and 1773 K (1500 °C) were examined by SEM. The SEM images of the quartz spheres presented in Figure 8 show cracks on the surfaces due to phase transformation of quartz into cristobalite which created stress within the spheres. Surface cracking exposed fresh surface of quartz to the reducing gas causing increase in the reduction rate, which explains fluctuations in the concentration of CO evolved in the reduction process.

(Figure 8)

Figure 9 presents the surfaces of the quartz spheres after reaction at different temperatures at a higher magnification. The surface of quartz was smooth before reaction; it was eroded and became porous after reaction at 1623 K (1350 °C) (Figure 9a). Development of the porous structure increased surface area. In the reduction at 1723 K (1450 °C) and 1773 K (1500 °C), a small amount of SiC particles was observed on the surfaces of quartz spheres (Figures 9b and 9c), which was confirmed by the EDS analysis. SiC was formed by the reaction of

deposited carbon with SiO. Amount of observed SiC particles in the sphere reduced at 1723 K (1450 °C) was higher than in the sphere reacted at 1673 K (1400 °C).

The surface of the sphere after reaction at 1773 K (1500 °C) was covered by SiC whiskers (Figure 9d). As studied previously [8–11], SiC whiskers in the reduction of quartz containing iron impurities were formed by the reaction of CH₄ and SiO under catalytic effect of iron or other transition metal elements, *i.e.* VLS (vapor-liquid-solid) mechanism. However, no catalyst globules were observed at the tip of SiC whiskers in this study, indicating that they were formed via VS (vapor-solid) mechanism occurred by gas-gas (SiO–CH₄) Reaction [9]. SiC whiskers were not found in the samples reduced at lower temperatures due to low SiO vapor pressure [12].

(Figure 9)

V. Conclusions

The reduction of quartz by methane-containing gas was studied in a laboratory fluidized bed reactor. A cold model was made which established the fluidization conditions of quartz powder. Direct reduction of quartz by CH₄–H₂ mixture is feasible, but in the temperature range of 1623 K (1350 °C) to 1773 K (1500 °C) proceeded to gaseous SiO. The initial rate of reduction increased with increasing temperature, fluidization gas flow rate (0.4–0.8 NL/min) and methane content in the reducing gas (below 5 vol pct). However, temperature above 1723 K (1450 °C) and methane content above 5 vol pct caused significant methane cracking and carbon deposition on the surface of quartz particles, which hindered further reduction. In the

reduction of quartz spheres at 1673 K (1400 °C) to 1773 K (1500 °C), a small amount of SiC was observed in the form of particles (1673 K (1400 °C) and 1723 K (1450 °C)) or whiskers (1773 K (1500 °C)).

Acknowledgements

This research was supported under the Australian Research Council Linkage Projects funding scheme (Project No. LP100100866). Commonwealth Scientific and Industrial Research Organization (CSIRO) provided quartz lumps crushing and grinding service. The electron microscopy characterization was carried out at the Electron Microscopy Centre (EMC) at the University of Wollongong.

References

1. A. Schei, J. Tuset, and H. Tveit: *Production of High Silicon Alloys*, Tapir Forlag, Trondheim, 1998.
2. S. Ranjan, S. Balaji, R.A. Panella, and B.E. Ydstie: *Comput. Chem. Eng.*, 2011, vol. 35 (8), pp. 1439–53.
3. D.H. Filsinger and D.B. Bourrie: *J. Am. Ceram. Soc.*, 1990, vol. 73 (6), pp. 1726–32.
4. J.G. Lee, P.D. Miller, and I.B. Cutler: *Reactivity of solids*, Plenum Press, New York, 1976.
5. N.S. Jacobson, K.N. Lee, and D.S. Fox: *J. Am. Ceram. Soc.*, 1992, vol. 75 (6), pp. 1603–11.
6. F. Aratani, Y. Sakaguchi, N. Yuge, M. Ishizaki, and T. Kawahara: *Bull. Jpn. I. Met.*, 1991,

- 1 vol. 30 (5), pp. 433–5.
- 2 7. E.H. Myrhaug and H. Tveit: *58th Electric Furnace Conference and 17th Process*
3 *Technology Conference Proceedings*, Warrendale, 2000, pp. 591–604.
- 4 8. U. Setiowati and S. Kimura: *J. Am. Ceram. Soc.*, 1997, vol. 80 (3), pp. 757–60.
- 5 9. H.J. Choi and J.G. Lee: *J. Mater. Sci.*, 1995, vol. 30 (8), pp. 1982–6.
- 6 10. J.V. Milewski, F.D. Gac, J.J. Petrovic, and S.R. Skaggs: *J. Mater. Sci.*, 1985, vol. 20 (4),
7 pp. 1160–6.
- 8 11. G. Urretavizcaya and J.M.P. Lopez: *J. Mater. Res.*, 1994, vol. 9 (11), pp. 2981–6.
- 9 12. X. Li, G. Zhang, R. Tronstad and O. Ostrovski: *Ceram. Int.*, 2016, vol. 42(5), pp. 5668–
10 76.
- 11 13. O. Ostrovski and G. Zhang: *AIChE J.*, 2006, vol. 52 (1), pp. 300–10.
- 12 14. T.C. Glayton: *Multiphase Flow Handbook*, CRC Press, Boca Raton, 2008.
- 13 15. A.C.D. Chaklader and A.L. Roberts: *J. Am. Ceram. Soc.*, 1961, vol. 44 (1), pp. 35–41.
- 14 16. G. Zhang and O. Ostrovski: *Metall. Mater. Trans. B*, 2000, vol. 31 (1), pp. 129–39.
- 15 17. X. Li, G. Zhang, K. Tang, O. Ostrovski and R. Tronstad: *Metall. Mater. Trans. B*, 2015,
16 vol. 46 (5) 2384–93.
- 17 18. R.A. Gardner: *J. Solid. State. Chem.*, 1974, vol. 9 (4), pp. 336–44.
- 18 19. G. Han and H.Y. Sohn: *J. Am. Ceram. Soc.*, 2005, vol. 88 (4), pp. 882–8.
- 19 20. J. Szekely, J.W. Evans, and H.Y. Sohn: *Gas-solid Reactions*, Academic Press, New York,
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5 (1450 °C); (d) 1773 K (1500 °C).

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Table I. Impurity contents in the quartz lumps, mg/kg

B	P	Fe	Al	Ca	Ti	Mn	Mg
0.5	1.0	33.0	219.0	26.0	7.9	1.9	27.0

Table II. Parameters of fluidization of quartz with different particle size ranges using pure nitrogen

Particle size (μm)	Calculated U_{mf} (m/s)	Calculated U_t (m/s)	Measured gas flow rate at U_{mf} (NL/min)	Measured U_{mf} (m/s)
53–100	0.0090	0.239	Fluidization was not observed;	N/A
100–140	0.0180	0.956	0.32	0.0170
140–200	0.0361	1.667	0.41	0.0220

1 Table III. Parameters of fluidization of 100–140 μm quartz particles by pure hydrogen at
2 different temperatures

Temperature	Calculated U_{mf} (m/s)	Calculated gas flow rate at U_{mf} (NL/min)	Calculated U_t (m/s)	Calculated gas flow rate at U_t (NL/min)
1623 K (1350 °C)	0.0113	0.036	0.545	1.728
1673 K (1400 °C)	0.0111	0.034	0.534	1.644
1723 K (1450 °C)	0.0109	0.033	0.524	1.566
1773 K (1500 °C)	0.0107	0.031	0.515	1.494

1 Table IV. Experimental conditions and extent of reduction of SiO₂ by CH₄–H₂ gas mixture
2 after reaction for 120 min

Sample	Temperature	Fluidization flow	Methane content	Weight loss	Reduction Extent
		rate (NL/min)	(vol pct)	(pct)	(pct)
1	1623 K (1350 °C)	0.8	5	7.8	4.4
2	1673 K (1400 °C)	0.8	5	29.0	25.0
3	1723 K (1450 °C)	0.8	5	38.1	32.0
4	1723 K (1450 °C)	0.4	5	20.0	18.2
5	1723 K (1450 °C)	0.6	5	28.4	24.8
6	1723 K (1450 °C)	0.8	2	21.9	18.6
7	1723 K (1450 °C)	0.8	10	8.3	4.6
8	1773 K (1500 °C)	0.8	5	31.2	26.2

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Fig. 1–Schematic of the fluidized bed reactor setup.

Fig. 2—Effect of temperature on the evolution of CO in the reduction of quartz by CH₄–H₂ gas mixture (5 vol pct CH₄) at gas flow rate 0.8 NL/min.

Fig. 3—XRD patterns of the samples reduced by $\text{CH}_4\text{-H}_2$ gas mixture (5 vol pct CH_4) at different temperatures after 120 min reaction.

Fig. 4—Effect of gas flow rate on the reduction of quartz by CH₄–H₂ gas mixture (5 vol pct CH₄) at 1723 K (1450 °C).

Fig. 5—Effect of methane content on the reduction of quartz by CH₄–H₂ gas mixture with flow rate 0.8 NL/min at 1723 K (1450 °C).

Fig. 6–Arrhenius plot calculated from peak rate of reduction at different temperatures.

Fig. 7—CO concentration in the off gas in the reduction of quartz sphere by the CH₄–H₂ gas mixture with 0.5 vol pct CH₄ at different temperatures. The gas flow rate was 1.6 NL/min.

Fig. 8—SEM images of quartz spheres after reduction by the CH₄–H₂ gas mixture with 0.5 vol pct CH₄ at: (a) 1723 K (1450 °C); (b) 1773 K (1500 °C).

Fig. 9–SEM images of the surface of quartz sphere after reduction by the $\text{CH}_4\text{--H}_2$ gas mixture with 0.5 vol pct CH_4 at: (a) 1623 K (1350 °C); (b) 1673 K (1400 °C); (c) 1723 K (1450 °C); (d) 1773 K (1500 °C).