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Version Post-print/Accepted Manuscript


Publisher's statement This is an Accepted Manuscript of an article published by Taylor & Francis in Canadian Metallurgical Quarterly on November 22, 2013, available online: http://www.tandfonline.com/10.1179/000844311X13117643274677

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Reduction Behaviour of Rice Husk Ash for Preparation of High Purity Silicon

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Abstract

The reduction of rice husk ash (RHA) silica for the preparation of high purity silicon was studied using magnesium as the reducing agent. Composite magnesium–RHA pellets with magnesium content varying from 0–25 wt% in excess of stoichiometry requirement were made and heated in the temperature range of 600–900 °C under flowing argon. It was found through differential thermal analysis (DTA) and temperature profile recording that the reaction of RHA silica with magnesium was triggered at about 575 °C. Quantitative XRD analyses of the reduction products showed that both initial magnesium content of the pellets and the reduction dwell temperature had a significant influence on the yield of silicon. In this study, a charge with 5 wt% magnesium in excess of the stoichiometric amount at reduction temperature of 900 °C gave a maximum silicon yield.

Keywords: RHA, silica, reduction, DTA, XRD, magnesiothermic silicon, solar grade silicon

1. Introduction

The search for novel low–cost methods for producing solar grade silicon for terrestrial photovoltaic power generation has been ongoing for decades. Solar grade silicon (sog–Si) refers to silicon material which impurity content of 0.01–1.0 ppmw (or 6–8N purity). The purity of SoG–Si is intermediate between metallurgical grade silicon (MG–Si) which is typically 98% and semiconductor grade silicon which is typically 9–11N purity[1, 2] Metallurgical grade and semiconductor grade silicon are respectively produced on commercial scale by the carbothermic reduction, and Siemens chemical vapour deposition processes. Thus much of the current research efforts to produce low cost solar grade silicon has evolved along these well established processes and can therefore be generally grouped into a metallurgical route and chemical vapour deposition route[3]. The vapour phase refining processes, which are essentially modifications of the Siemens process, succeed in making the silicon highly pure but prohibitively expensive for solar PV applications. The metallurgical route which is believed to be a cheaper alternative has not been effective in reducing dopant impurities such as boron (B) and phosphorus (P) to the sub–ppmw levels generally accepted for manufacture of efficient solar cells. Boron and phosphorus together with other electro–active impurities are incorporated into the MG–Si via quartz or a

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quartzite raw material which is used as silica source in the carbothemic reduction process. The boron content of as–produced MG–Si lies in the range of 10–50 ppmw whilst the phosphorus content range from 20–40 ppmw [4].

For the metallurgical route to SoG–Si to be effective, the growing consensus has been to use very high purity silica and reducing agents that are almost free of boron and phosphorous.[5] The need for purer sources of silica has therefore provoked interest in silica from sources other than geologic quartz or quartzite rocks. It is against this background that amorphous silica in rice husk ash (RHA) is being explored for the possibility of producing a SoG–Si feedstock material.

Rice husk ash (RHA) is the residual product after combustion of rice husks – an agricultural waste which is in abundant supply throughout many parts of the world. The amount of amorphous silica in RHA is estimated at 87–97% with a relatively narrow range of metallic oxide impurities.[6] The amorphous nature of RHA makes it more reactive than crystalline silica and therefore more amenable to purification treatments and reduction by reactive metals. A few feasibility studies on producing solar grade silicon from amorphous silica in RHA by metallothermic reduction have been attempted. Singh and Dindhaw [7] reported obtaining silicon of 6N purity by reducing white rice husk ash with magnesium at a temperature of 800 °C followed by a series of acid leaching steps. Subsequently Bose et al. [8] investigated magnesium reduction of rice husk ash at a temperature of 600–650 °C but obtained silicon with purity significantly less than that reported by Singh and Dhindaw. The magnesium reduction of rice husk ash to produce silicon has also been investigated by Banerjee et al. [9] and by Ikram and Akhter [10]. Banerjee et al. reduced acid leached rice husk ash by intimately mixing the ash with magnesium powder and firing the powder mixture in a sealed graphite crucible in a muffle furnace. Following a similar approach but with 4N magnesium purity, Ikram and Akhter reported reduction of rice husk ash at a temperature of 620 °C to yield silicon of 99.95% purity after acid leaching purification steps.

Previous research on reduction of RHA with magnesium have been carried out only at fixed or limited temperature range and fixed reactant composition. The focus of this study therefore is to investigate the effect of temperature and initial reactants composition on the yield of silicon in the reduction product and to develop an understanding of the mechanism of the reduction process. Results of a two stage purification of the silicon by acid leaching will also be presented.

2. Theoretical Considerations

For the reduction of RHA silica by magnesium, possible overall reactions that result in the formation of various compounds may be summarised by Eqs. (1)–(5):

\[
\begin{align*}
\text{SiO}_2(s) + 2\text{Mg}(s) &= \text{Si}(s) + 2\text{MgO}(s) \quad \Delta G^{\circ}_{298K} = -282 \text{ kJ/mol} \\
\text{Si}(s) + 2\text{Mg}(s) &= \text{Mg}_2\text{Si}(s) \quad \Delta G^{\circ}_{298K} = -75 \text{ kJ/mol} \\
\text{SiO}_2(s) + 2\text{MgO}(s) &= \text{Mg}_2\text{SiO}_4(s) \quad \Delta G^{\circ}_{298K} = -63 \text{ kJ/mol} \\
\text{SiO}_2(s) + 2\text{Mg}(g) &= \text{Si}(s) + 2\text{MgO}(s) \quad \Delta G^{\circ}_{298K} = -507 \text{ kJ/mol} \\
\text{Si}(s) + 2\text{Mg}(g) &= \text{Mg}_2\text{Si}(s) \quad \Delta G^{\circ}_{298K} = -300 \text{ kJ/mol}
\end{align*}
\]
The reduction of silica (SiO\textsubscript{2}) by magnesium (Mg) in this work was first studied theoretically using the FactSage™ thermodynamic package [11] to examine the effects of process variables such as temperature and magnesium to silica ratio on the equilibrium amounts of the phases that are formed in the reaction products.

3. Experimental

Rice husk ash used in this study was obtained from Process Research Ortech Inc. (Ontario, Canada). The specific surface area of the as–received RHA was determined using Coulter SA 3100 Analyzer with nitrogen as the adsorbate gas and the BET calculation model[12]. The particle size distribution was determined with a laser diffraction particle size analyzer (Malvern Master Sizer S). The chemical composition of RHA was determined by digestion combination of ICP–MS and Leco carbon analyzer. The morphological features of the RHA sample were examined by scanning electron microscope (Hitachi S2500).

Subsequently, the as–received RHA was subjected to purification treatment by leaching in 10 wt% HCl at 90 °C for 4h followed by roasting in air at 700°C for a period of 1–2h to obtain silica content of approximately 98 wt%. The purified RHA and magnesium granules (98 wt%, Sigma Aldrich) mixture in predetermined weight ratios were wet blended with 4% polyvinyl alcohol solution (98–99 wt%, Fischer) and briefly dried under an argon atmosphere. The dried reactants were compacted under 4000 kgf into 16 mm diameter cylindrical pellets. The porosity of the pellets was determined by considering the bulk density of the pellets relative to their theoretical density, and was found to be about 40% on average.

The charge composition was formulated based on pure stoichiometric silica and the overall reaction presented in Eq. (1). For a fixed weight of SiO\textsubscript{2}, the effect of Mg/SiO\textsubscript{2} ratio was investigated by varying the magnesium content in the charge from 0–25 wt% in excess of the stoichiometric amount

The reduction experiments were carried out under argon atmosphere at selected temperatures in the range of 600–900°C with the aid of the experimental set–up as shown in Fig. 1. The equipment consisted of a Lindberg horizontal tube furnace with a recrystallized alumina work–tube of inner diameter 54 mm. The temperature was measured using data logger thermometer (Omega HH306A) and a K–type thermocouple that was located close to the charge.

The sample temperature was ramped at the rate of 10 °C/min, then held at the target temperature for 1h and then allowed to naturally cool to room temperature. The reduction product from each experiment was hand milled using alumina mortar and pestle till 100 % passing Tyler sieve # 50 (300 µm). Subsequently, samples were taken and further milled to ‘talc powder’ fineness for quantitative XRD analyses.

Purification of the bulk reduction product passing 300 µm was carried out by two acid leaching steps. The first stage leaching was carried out using mixture of 1.25M HCl and 4.37M
CH₃COOH (acetic acid) in a respective volume ratio of 4:1 at temperature of 70 °C for a period of 1h. The leached residue obtained after vacuum assisted filtration was thoroughly washed with de–ionized water, dried and then subjected to a second stage leaching.

The reagent for the second stage leaching comprised a mixture of 2.76M HF and 4.37M CH₃COOH (acetic acid) in a volume ratio of 1:9 respectively. Leaching time and temperature were respectively kept at 1h and 70 °C.

**Fig. 1**: Schematic diagram of reduction facility.

### 3.1 Analysis of Reduction Reaction Product

Phases present in the reduction product were identified using Philips X–ray Diffractometer (model PW3710). The phases identified in the XRD pattern of each reduction product sample were quantified by Rietveld method as described by Young and Cox [13]. The Rietveld method is a whole pattern fitting method which uses crystal structure data and peak profile information to generate and fit calculated XRD patterns to experimentally determined spectrum by means of least squares refinements [14].

### 3.2 Reduction Reaction Mechanism

The mechanism of the reduction reaction between RHA silica and magnesium was studied by differential thermal analysis (DTA). The analysis for a stoichiometric mixture of purified RHA and magnesium was conducted using an NETZSCH STA 409 PC/PG facility. A 48 mg sample was loaded into the DTA alumina crucible and with a certified alumina material as a reference; heating was initiated at a rate of 5 °C/min from 35 °C to 1150 °C with a continuous flow of argon.

To investigate the possible effect of sample mass, a sample significantly larger than the DTA mixtures was compacted into a hollow, donut–shaped pellet of the reactants having a fixed composition and weighing about 1.8g. The pellet was fitted with a thermocouple placed at its core and was suspended in the hot zone of a modified version of the experimental set–up shown in Fig.1. One end of the furnace tube was fitted with a water cooled stainless steel cap containing a glass window that was aligned with a high definition imaging camera which captured the progress of the reduction reaction.

### 4. Results and Discussion

#### 4.1. Characteristics of RHA

The characteristics of the as–received RHA and the treated RHA samples are shown in Table I. The BET specific surface area of 39 m²/g is slightly higher than the 36.44 m²/g reported by
Srivastava et al.[15] who characterized their as–received RHA to be mesoporous. Also, the average RHA particle size of 35µm found in this study is significantly lower than the ≈150µm of the RHA sample characterized by Srivastava et al. The difference in surface area and particle size of a particular rice husk ash sample can be attributed to the rice husk combustion technique employed. One can also notice from Table I that the silica content of the treated RHA had increased by about 7 wt% with a corresponding decrease in the metallic oxide and carbon content. This increase in silica content of the treated RHA sample is comparable to the results obtained by Shinohara and Kohyama[16] who obtained an increase in the silica content of their RHA sample from 92.95 wt% to 96.94 wt% after leaching with hydrochloric acid.

Table I – Characteristics of as–received rice husk ash

The morphology of the RHA as determined by SEM is shown in Fig. 2. As can be seen from the SEM micrograph in Fig. 2, the as–received RHA reveals multifaceted honeycomb particle morphology. The pores in the honeycomb structure are attributed to the thermal decomposition of organic matter during combustion of rice husk. According to Genieva et al.[17], the decomposition of organic matter from RHA imparts high porosity and relatively large specific surface area as shown in Table I. The XRD pattern of the as–received RHA showed a broad peak spanning Bragg’s 2θ angle range of 18–30⁰ which is characteristic of amorphous structures[18]. The combination of relatively large surface area, high porosity and amorphous crystal structure thus makes RHA amenable to simple purification treatment when compared to quartz.

Fig. 2: SEM micrograph of as–received RHA.

4.2 Effect of initial charge composition on phases in reduction product

The XRD patterns shown in Fig.3 indicate the effect of initial magnesium content on the phases found in the reduction product at 650°C. Qualitatively, it can be seen that the peak intensity for the Mg₂Si phase increases with increase in excess magnesium whereas the peak intensity for Si decreases. In particular the peak intensity of Mg₂Si appears relatively smaller at 5 wt% excess magnesium while the inverse for Si is true. Above 5 wt% excess magnesium, the intensity of the silicon peaks appears to diminish. The quantitative phase analyses of the reduction products are shown in Table II. From the data in this table, Si yield defined as the ratio of elemental silicon in the reduction product to the total silicon content in the initial silica of the charge.

Fig.3: XRD patterns comparing the effect of excess magnesium on the phases formed (● Si , ○Mg₂Si).

Table II – Composition of the reduction products
As shown in Fig. 4, the Si yield goes through a maximum with increasing magnesium to silica mole ratio. The maximum silicon yield occurs with a charge composition having 2.1 mole ratio of magnesium to silica or alternatively a charge with 5 wt% excess magnesium when reduction is carried out in an inert atmosphere. In this figure is also included the theoretical yield of Si calculated from equilibrium conditions. As seen, increasing Mg above its stoichiometric amount should reduce the Si production. Fig. 4 shows the composition of the reaction products under equilibrium conditions. It is evident that any excess Mg will form Mg$_2$Si at the cost of Si, thus lowering the Si yield. It may be therefore concluded that the reactions did not proceed to equilibrium under the experimental conditions, presumably because of kinetic limitations. It is therefore interesting to examine the effect of temperature on the extent of the reactions.

**Fig. 4** Effect of Mg/SiO$_2$ ratio on Si yield at 650 °C.

### 4.3 Effect of temperature on phases formed in reduction product

The effect of temperature on the relative amount of phases formed with a magnesium–RHA charge having 5% excess magnesium is qualitatively compared in the XRD pattern in Fig. 5. The peak intensity of silicon in Fig. 5 is observed to increase with increasing temperature while that of the Mg$_2$Si phase diminishes with increasing temperature. The results of the Rietveld quantitative phase analysis of the reduction samples whose XRD patterns appear in Fig. 5 are plotted as a function of temperature in Fig. 6. It is found that the yield of silicon increases with temperature and this is achieved due to reduction in the amount of Mg$_2$Si. Thermodynamic evaluation of the effect of temperature (Fig. 7) shows similar trends in both Si yield and Mg$_2$Si amount, although the absolute values are not consistent with the experimental measurements. At higher temperature, the experimental results approach the theoretical values, indicating faster reaction kinetics as the temperature increases.

**Fig. 5:** XRD pattern comparing effect of temperature on amount of phases formed with a charge mix containing 5% excess magnesium. ● Si ○Mg$_2$Si.

**Fig. 6:** Experimentally measured effect of temperature on (a) Mg$_2$Si formation and (b) Si yield with a charge mix containing 5% excess magnesium.

**Fig. 7:** Thermodynamic evaluation of the effect of temperature on the equilibrium products for a charge mix with 5% excess Mg.
4.4 Mechanism of reduction reaction

The result of differential thermal analysis (DTA) carried out on a powdered mixture of magnesium and purified RHA containing 5wt % excess magnesium is shown in Fig. 8a. The figure shows multiple heat release peaks labeled as A, B and C. Peak A has an onset temperature of 524.2 °C and a peak temperature of 540.8 °C. The two major peaks B and C have onset temperatures of 573.8 and 643.8 °C and peak temperatures of 590.4 and 647.9 respectively.

The temperature–time plot for the hollow magnesium–RHA disc pellet having an initial composition of 5wt % excess magnesium and weighing 1.8g is given in Fig. 8b. In comparison with the DTA profile, only one major heat release peak for the pelletized reactants is recorded by the thermocouple. The onset temperature of 575 °C is close to the onset temperature of 573.8°C for the heat release peak B in Fig. 8a. It is also seen that this peak is followed by a gradual heat release that continues for the remainder of the experiment. The pellet conditions immediately before and after the onset of the heat release peak are shown in Fig. 9. The appearance of pores on the surface of the reacted pellet is an indication of the conversion of low density reactants to a relatively high density reaction product with a corresponding decrease in volume.

**Fig.8:** (a) DTA diagram for a magnesium–RHA powder mixture (b) temperature profile during heating of the ‘donut’ magnesium–RHA pellet

**Fig.9:** Pellet condition before and after on–set of reaction.

The effect of temperature and reactant mix ratio on the products may be explained using a reaction path proposed below.

Magnesium is one of the metals with a relatively high vapour pressure. A thermodynamic evaluation of the Mg–SiO<sub>2</sub> system (Fig. 10) shows that for any temperature in the range 0–1100 °C, the equilibrium vapour pressure of pure magnesium is greater than that required to reduce SiO<sub>2</sub> (i.e. moving reaction (4) forward). It implies that the reduction by Mg gas of silica is thermodynamically feasible. From kinetic point of view, the reduction by Mg gas can proceed at substantially higher rates than the reactions involving solid/liquid Mg. Therefore, it may be suggested that for the rapid reactions observed in this work, reduction takes place primarily through gaseous Mg.

**Fig.10:** Vapour pressure of magnesium required for reduction of SiO<sub>2</sub> (solid line) and in equilibrium with pure Mg (dashed line).

According to Banerjee et al. [9], Mg can sublime at temperatures as low as 400 °C. As the temperature of the mixture increases, the vapour pressure of magnesium inside the composite
pellet increases. Eventually at temperatures around 575 °C, the vapour pressure is high enough so that an exothermic reaction involving gaseous Mg can be triggered. This temperature is consistent with the self–ignition temperature of Mg found by Popov [19]. He has reported ignition temperatures of 540 –585 °C in dry air, depending on the particle size and shape. It may therefore be postulated that in the RHA–Mg composite pellets, the ignition is triggered in the vicinity of the pockets of air trapped inside the closed porosity of the sample. This reaction starts when the sample temperature is around 575 °C, which is consistent with the results obtained from both the DTA and hollow–pellet experiments.

As the exothermic reaction proceeds, local temperatures are increased, resulting in more supply of magnesium vapour. The reaction between trapped air and Mg vapour may be very quick due to the small volume of air and the rapid nature of gas–gas reaction. However, the fast heat release should be sufficient to increase the localized Mg pressure. The gas–solid reaction between Mg and SiO$_2$ can take place at much higher rates compared to an alternative solid–solid reaction. In addition, the reduction reaction is exothermic, thus is self–accelerated. As shown in Fig. 10, the energetic wave propagation due to exothermic reaction at onset causes a fraction of the suspended pellet to be broken away.

The initially rapid reaction is however slowed, as the reduction products, MgO and Si limit diffusion of Mg to the SiO$_2$ core. This creates a concentration gradient for Mg from the surface to the reaction interface. Therefore, at the outer layers the thermodynamic conditions become favourable for formation of Mg$_2$Si

Further reduction of SiO$_2$ is made possible by diffusion of Mg through the sandwiched product layer, composed of Mg$_2$Si, MgO and Si. Also, insufficient Mg at the SiO$_2$/MgO interface favours formation of Mg$_2$SiO$_4$ rather than reduction of SiO$_2$.

The reaction thus becomes diffusion controlled so that higher temperature and longer time (due to heating to higher temperatures) favour further reduction of SiO$_2$, leading to the consumption of Mg$_2$Si with resultant higher Si yield and lower Mg$_2$Si formation as observed in the Rietveld quantitative XRD results shown in Fig.6. The reduction reaction continues to release heat, but at a slower rate, thus a gradual increase in the temperature of the sample is seen. It is to be noted that peak C in Fig. 8 (a) is related to melting of magnesium that is spread over the un–reacted silica, thus promoting a quick transient reaction. This peak is not observed in the hollow–pellet test. It is believed that this is because for this larger batch (compared to the very small 48 mg DTA sample), heat loss from the sample is smaller, thus sufficient heat from the initial gas–solid reaction exists to evaporate magnesium adequately so that the SiO$_2$ particles are reduced at the surface. Consequently, if any Mg is left after the reaction commences, it will not come in direct contact with SiO$_2$, (but rather with Mg$_2$Si layer). Therefore, in this case melting of the remaining magnesium is not followed by an exothermic reaction.
Based on this reaction mechanism, it is suggested that smaller RHA particles, higher operating temperature and longer dwell time (or slower cooling) will result in higher yield of Si. Operating under these conditions will also decrease the Mg consumption.

5. Silicon Product from RHA Reduction

The purity of two batches of silicon produced by this process is presented in Table III and compared to silicon typically used for the Czochralski (CZ) crystal pulling for ultra high purity silicon applications.

Table III – Comparison of chemical composition of Si from this study to Si for CZ pulling

It is seen from Table III that the purity of the silicon obtained surpasses the purity specification of industry standard silicon thus it can potentially be refined by additional well known metallurgical processes to achieve solar grade silicon specification.

5.1 Summary and Conclusions

In this work, the reduction behaviour of RHA and magnesium for the preparation of high purity silicon has been studied theoretically and experimentally. Initial charge composition in terms of percent excess magnesium and reduction hold temperature were found to influence the yield of silicon. A charge with 5 wt% excess magnesium and reduction temperature of 900 °C in an argon atmosphere gave maximum silicon yield. The reaction between magnesium and SiO$_2$ in rice husk ash is initiated when the temperature reaches around 575 °C, at which temperature Mg has sufficiently high vapor pressure. The self–accelerating reaction proceeds by forming a sandwiched layer of MgO and Si at the surface of the original silica particles. Further reaction proceeds by diffusion of the reactants through this layer, where at the outer layers, silicon reacts with Mg to form Mg$_2$Si. The decrease in magnesium silicide amount with increasing temperature and resultant increment in silicon yield is consistent with a reduction reaction that is diffusion controlled.

Acknowledgements

The authors wish to acknowledge financial support and technical assistance provided by Process Research Ortech Inc. Additional financial support from Ontario Centers of Excellence and the University of Toronto Open Fellowship is hereby acknowledged. We wish to acknowledge Karim Danei (PhD candidate, Ryerson University, Department of Materials Science and Engineering) for his assistance with the experimental set–up.
References

### Tables and Table Captions

#### Table I – Characteristics of as–received rice husk ash

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<th>Samples</th>
<th>As–received RHA</th>
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*Main oxide components determined by ICP analyses

#### Table II – Composition of the reduction products

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Table III – Comparison of chemical composition of Si from this study to Si for CZ pulling

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Figures and Figure Captions

Fig. 1: Schematic diagram of reduction facility

Fig. 2: SEM micrograph of as–received RHA.
Fig. 3: XRD patterns comparing the effect of excess magnesium on the phases formed (● Si, ○Mg$_2$Si).

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