Effect of H₂ on SiO and SiC formation

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Abstract

Based on previous research, hydrogen has an enhancing effect on the kinetics of the Si-O-C system [1-3]. In this study silicon carbide (SiC) formation, from a reaction between SiO(g) and carbon, were investigated in a hydrogen atmosphere, an argon atmosphere, and an argon atmosphere containing 10% methane, at temperatures between 1495 °C and 1695 °C. The SiO(g) was generated from pellets comprised of a 2:1 ratio of silica (SiO₂) and SiC. The SiO(g) generation was monitored through analysis of the CO(g) content of the off-gas, the results indicated that the hydrogen atmosphere had an enhancing effect on SiO(g) generation through this reaction. Samples were retrieved from various locations within the set-up: the crucible, the reaction chamber roof, and from the condensation chamber. The reaction products were imaged in SEM using secondary electrons.

SiC was found growing throughout the reaction chamber, when using an argon atmosphere, a layer of SiC was found covering the graphite parts, whereas utilising a hydrogen atmosphere, or argon with 10% methane, the SiC would instead grow as whiskers. Thermal decomposition of methane is expected to be a challenge in this temperature range [4].

Keywords: silicon, SiC, hydrogen, methane, whiskers

Kulcsszavak: szilícium, SiC, hidrogén, metán, whisker

1. Introduction

Silicon is currently produced in a submerged arc furnace from a reaction between SiO₂ and carbon. SiO₂ is supplied from high purity quartz, and commonly used carbon sources include: wood chips, charcoal or coal [5]. One of the most important intermediate species occurring during silicon production is SiO(g). It is formed in the hot lower region of the furnace from a reaction between SiO₂ and silicon carbide (SiC), reaction (1), and is consumed in the cooler upper region where it reacts with the carbon in the charge to form SiC, reaction (2). When SiO(g) is cooled down it will form Si and SiO₂ according to reaction (3), it may also form SiO₂ and SiC according to reaction (4). These reactions are commonly called the condensation reactions [5-6].

Producing silicon consumes large amounts of energy. It is supplied, in part, from electricity, and in part from solid carbon materials. Finding a replacement to the carbon materials could lead to significant reductions in CO₂ emissions. Thus far there has been some research into possible alternatives to carbon for reducing metal oxides [7-9]. Most of the work has been on the use of methane hydrogen mixtures [10-11]. Despite the fact that CH₄(g) contains carbon, which will lead to CO₂(g) emissions, it may allow a more efficient process to be designed, or if bio-gas was utilised the net-CO₂(g) emissions would also be lowered. While some metals, such as iron, may be readily reduced to its

metallic form by hydrogen, silicon has a much stronger affinity to oxygen making the reduction process more challenging [9]. One of the key challenges that face the use of CH₄(g) in silicon production is that the gas is unstable at high temperatures, and will undergo thermal cracking to H₂(g) and carbon according to reaction [4]. According to its thermodynamic equilibrium, CH₄(g) will be almost completely transformed to carbon and H₂(g). However, literature reports that methane cracking often occurs far away from its thermodynamic equilibrium if it does not happen on a suitable catalyst [12]. Furthermore, the deposited carbon is a poor catalyst for this reaction, so as CH₄(g) cracks it will form a layer which limits further cracking [4], [13]. Similarly, SiO(g) will form a condensate at low temperatures. Thus, there is a large temperature gap between the regions where each of the gasses are stable. Therefore, it is important to research how far away from their respective equilibrium pressures it is possible to go.

This study aims to investigate the reaction between SiO(g) and carbon, and how it is influenced by different hydrogen containing atmospheres. In addition, the extent of thermal cracking of CH₄(g) will be examined, and whether it is possible to have CH₄(g) and SiO(g) react.

2. Experimental

SiO(g) and CO(g) were produced from pellets made from pure quartz and pure SiC which was crushed to a size of 5 mm. The quartz and SiC was pelletized and mixed with a molar ratio of 2:1, which follows the stoichiometry of reaction (1). A

schematic drawing of the set-up is shown in Fig. 1. It consists of two main parts: a reaction chamber which is the bottom section, and a condensation chamber which is the top section. The reaction chamber contained a graphite crucible, which was filled with approximately 5 g of pellets before each experiment. An alumina lance was inserted into the reaction chamber from the top of the set-up. The condensation chamber consisted of a graphite tube surrounded by graphite wool insulation. While preparing the experiment, the alumina tube was placed through the middle of the condensation chamber in such a way that it protruded 2.5 cm into the reaction chamber. Additionally, a C-type thermocouple was passed through the lance so that its tip was in the center of the reaction chamber. After inserting the lance, SiC particles were poured into the space between the lance and the condensation chamber wall, which were added to collect reaction products.

After the set-up had been prepared according to the description in the previous paragraphs, it was placed into the furnace. The furnace was a resistance heated vertical tube furnace. The off-gas from the furnace went through a gas analyser which detected the CO(g) content. First, the furnace was flushed with argon and evacuated down to 180 mbar, then it was refilled with argon as the temperature program commenced.

Fig. 1 Set-up used to investigate the reaction between the SiO(g) and CO(g), and carbon in an Ar(g) and an H₂(g) atmosphere

1. ábra A SiO(g) és CO(g), valamint a szén reakciója Ar(g) és H₂(g) atmoszférában

The temperature measured within the reaction chamber was observed to be lower than the furnace set-point, which was 1750°C, 1650°C or 1550°C. Fig. 1 shows the temperature measurements from the reaction chamber. It shows that the real temperature in the reaction chamber is around 55°C lower than the set-point of the furnace, the thermocouple is measuring the temperature in the centre of the reaction chamber. The parameters which were varied between experimental runs were the holding temperature, which was either 1595°C, 1695°C, or 1495°C and the process gas mixture which was a H₂(g)/CH₄(g) gas mix that was varied between 0% CH₄(g) and 10% CH₄(g). The experimental matrix displayed in Table 1 shows the number of experiments performed for each combination of parameters. After each experiment, samples

were taken from various regions of the set-up. They were taken from the crucible rim, the ceiling of the reaction chamber, the graphite ring on the bottom of the condensation chamber, the alumina lance, and SiC chunks in the condensation chamber. The samples were placed into a SEM and imaged with a secondary electron detector.

	Methane content in a CH ₄ (g)/Ar gas mix		
	Pure H ₂ (g)	0%	10%
1695°C	2	1	0
1595°C	2	1	1
1495°C	0	1	0

Table 1 Experimental matrix, the number in each cell indicates number of parallels
1. táblázat Kísérleti mátrix, az egyes cellákban szereplő számok a párhuzamok számát jelzik

3. Results/Discussion

3.1 Generation of SiO(g) from the raw material

Fig. 2 CO(g) content of the off-gas for experiments in an Ar atmosphere at various temperatures

2. ábra A kiáramló gáz CO(g)-tartalmának vizsgálata Ar atmoszférában, különböző hőmérsékleteken

Fig. 3 CO(g) content of the off-gas for experiments in an H₂(g) atmosphere at various temperatures

3. ábra A kiáramló gáz CO(g)-tartalmának vizsgálata H₂(g) atmoszférában, különböző hőmérsékleteken

Isothermal experiments in an argon/CH₄(g)/H₂(g) atmosphere were performed. The reaction was monitored through measurement of the CO content of the off-gas. Fig. 2 shows the off-gas measurements for the experiments in an

argon atmosphere at 1495°C, 1595°C and 1695°C. Fig. 3 shows the off-gas measurements for the experiments in a H₂(g) atmosphere at 1595°C and 1695°C.

Fig. 4 Normalised integral CO(g) formation during experiments in pure H₂(g), Ar(g) and Ar with 10% CH₄(g), at 1595°C

4. ábra Normál integrált CO(g) képződés vizsgálata tiszta H₂(g), Ar(g) és Ar 10% CH₄(g) összetételű atmoszférában 1595°C-on

Fig. 4 shows a comparison of the normalised integral CO(g) content of the off-gas, with H₂(g), Ar, and Ar with 10% CH₄(g), at 1595°C. The most obvious trend of the off-gas CO(g) content is that it increases with temperature, at least in an Ar(g) atmosphere. Which is an indication of the raw material being converted to SiO(g) and CO(g) at a more rapid pace. However, when the atmosphere is exchanged with pure H₂(g), the effect of temperature is not so obvious. Furthermore, after the initial peak in the CO(g) content, the curves follow each other closely for the rest of the temperature program. Thus, as a result of using an H₂(g) atmosphere, the SiO(g) content in the reaction chamber is increased.

The weight of the pellets which were recorded before and after each experiment are consistent with what was seen in the CO(g) content of the off gas. Table 2 shows what weight change was seen at different temperatures and atmospheres, evident that much more of the pellets were transformed to SiO(g) in an H₂(g) atmosphere than in Ar(g).

Temperature	Mass change in Ar(g)	Mass change in H ₂ (g)
1695°C	-	-57.9%
1595°C	-14.4%	-45.7%
1495°C	-12.4%	-

Table 2 Mass change of the raw material for each experiment

2. táblázat A nyersanyag tömegváltozása a kísérleteknél

3.2 Formation of SiC

SiC crystals could be seen growing in the rim of the graphite crucible. At the cooler temperature, the crystals are much smaller and large ones are more sparsely distributed on the surface. In an H₂(g), or Ar(g) with 10% CH₄(g) atmosphere the surface of the crucible is covered in SiC whiskers. Growth of SiC whiskers in H₂(g) containing atmospheres has been seen previously. The most common explanation for growth of SiC in H₂(g) containing atmospheres is that presence of hydrogen allows CH₄(g) to form in small quantities. This would allow for an enhanced gas phase transfer of carbon which is necessary to

grow long SiC whiskers [1], [14]. Improved diffusion in H₂(g) may also contribute. Reaction (6) and (7) show how CH₄(g) might provide a means for gas phase carbon transfer to the whisker tips.

In Si containing systems the growth mechanisms of whiskers most often cited are vapour-liquid-solid (VLS), where there is a liquid impurity that acts as a catalyst to the whisker growth, vapour-solid (VS) where there is no catalyst, and oxide assisted growth (OAG) where there is layer of molten SiO₂ around the tip [15]. However, regardless of which of these growth mechanisms are present in this work, all of them require gas phase transfer of carbon from the graphite parts to the whisker tip. The two options are through CO(g)/CO₂(g) or H₂(g)/CH₄(g). Considering that the equilibrium CH₄(g) pressure is larger by a factor of 1000, compared to CO₂(g), in this temperature range H₂(g)/CH₄(g) is expected to play a bigger role [16-17].

4. Conclusions

The H₂(g) atmosphere had an enhancing effect on the SiO(g) formation in the raw materials. Additionally, the SiO(g) formation in an H₂(g) atmosphere was much less affected by temperature than in a pure Ar(g) atmosphere.

SiC formation in the current experimental set-up was enhanced in an H₂(g) atmosphere compared to an Ar(g) atmosphere. There are a few possible explanations, the presence of H₂(g) allowed for a kinetically more favoured reaction path to SiC formation. The increased SiO(g) formation leads to a higher SiO(g) content throughout the reaction chamber which would increase SiC formation. Faster diffusion in the H₂(g) atmosphere may also play a role in the improved kinetics. Furthermore, the SiC formed in an H₂(g) atmosphere grew as whiskers, while in an Ar(g) atmosphere it grew as a layer covering the graphite. The difference is suspected to be caused by the formation of CH₄(g) from the H₂(g) reacting carbon, and the CH₄(g) allows for fast gas phase carbon transfer to the whisker tip.

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