Sintering Mechanism of silicon from K_2SiF_6 -Al

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Abstract. In order to clarify the reaction process of Si phase, Differential Scanning Calorimeter (DSC), as the main measurement, was used to prepare Si samples and monitor the sintering reaction process. Combined with X-ray diffraction analysis, the formation process of Si phase was summarized. The reaction between K_2SiF_6 and Al powders occurred at 580°C, but not completed until 660°C. The whole formation process of Si includes two different stages: One is the solid–solid reaction stage, the other is the solid–liquid reaction stage.

1 Introduction

Silicon does not exist in the spontaneous world, at present, silicon is the raw material of production of silicone. Preparation of silicon powder has become a research focus. Many reports have been devoted to exploring the technique of producing silicon [1-4]. Silicon is normally produced by carbothermic reduction [5]. Silane SiX_4 (Cl, Br, I) reduced by hydrogen or metal is also a silicon production way. In addition, molten salt electrodeposition is another silicon production method [6]. D. Elwell reported that silicon could be get from K_2SiF_6 -flinak by electrodeposition [6, 7]. Now, carbothermal reduction is widely used industrial-scale production method.

However, Si-O bond is one of the most stable chemical bonds in the nature. To activate or cleave SiO_2 , its high bond energy needs to be overcome. Carbon thermal reduction occurs at 1200°C, therefore, carbon thermal reduction is a high energy consumption method. Potassium silicon fluoride and aluminum powder are used to produce silicon in this paper. The potassium silicon fluoride is a byproduct of production potash fertilizer using potash feldspar. This study can realize waste recycling and also provide an important information for the silicon phase formation process.

The aim was to focus on the mechanism in the synthesis of silicon through the reaction between potassium silicon fluoride and aluminum powder, by X-ray diffraction and the Differential Scanning Calorimeter (DSC).

2 Materials and methods

2.1 Samples

Silicon samples were prepared by the solid-state reaction method using potassium silicon fluoride and aluminum

powder as the raw materials. Potassium silicon fluoride and aluminum (200 mesh size) were all in powder form. The weight ratio between the Potassium silicon fluoride and aluminum was kept at 1:0.2 in all the experiments. All powders were thoroughly mixed before using.

2.2 Sample characterization

High-temperature Differential Scanning Calorimeter (DSC) (SDT Q600 V8.0 Build 95) was carried out on the mixture of potassium silicon fluoride and aluminum powder. The DSC was carried out at normal atmosphere in the temperature range of 20°C - 800°C (silicon easily oxidized before 800°C) [8], with a heating rate of 15°C/min.

Based on the DSC results, the samples were then subjected to process at different temperatures using porcelain crucibles in muffle furnace and were further characterized by X-ray diffraction (XRD). Phase changes were monitored using a Rigaku D/MAX-rA X-ray diffraction (XRD) machine with Cu $K\alpha$ radiation, operated at 40kV and 40mA. The scanning speed used was 8 deg/min on the sinter.

Four different sintering temperatures of 570°C, 580°C, 600°C and 670°C for 1h, respectively, were selected according to successive heating DSC curve up to 800°C (see Fig. 1). The samples were heated in the normal atmosphere at these temperatures. The heating rate was 15°C/min during sintering process.

3 Results and discussion

3.1 DSC analysis

Fig. 1 shows the DSC results of a mixture of potassium silicon fluoride and aluminum powders. Apart from the exothermic peaks at 580°C and 600°C associated, an

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endothermic peak at 660 °C (the melting point of pure aluminum) was detected.

According to the DSC curves, the reaction between K_2SiF_6 and Al powder started at about 570°C, and then a stronger exothermic peak (Fig. 1, peak 1), caused by the formation of $KAlF_4$ and K_3AlF_6 , appeared. The subsequent gentle exothermic peak (Fig. 1, peak 2), caused by Si formed, is smaller than the peak 1. The

endothermic peak (Fig. 1, peak 3) was caused by pure aluminum melted. After Al melted, the reaction between the K_2SiF_6 and fused Al powder became stronger than that in the first two stages as the liquid phase (Al) increased diffusion rate of atom and enlarged the contacting area of reactants [9]. This indicated that the reaction between K_2SiF_6 and Al powder did not complete before Al melted.

Fig. 1 DSC curve of mixture of K_2SiF_6 :Al=1:0.2 (black line), heated at a rate of 15 °C/min

Reactions exhibit different mechanism. One belongs to solid–solid reaction, the other is solid–liquid reaction according to whether there is fused Al or not during the process.

In order to identify the phase formed at different stage, four different sintering temperatures of 570 °C, 580 °C, 600 °C and 670 °C, for 1h were selected corresponding to the different stages of DSC curve in the sample with a mixture of K_2SiF_6 :Al=1:0.2 (see Fig. 1). X-ray diffraction patterns of the samples obtained after heating treatment at different temperatures mentioned above are shown in Fig. 2 (a, b, c, d, e).

3.2 Formation of phase and identification

Fig. 2a

Fig. 2b

Fig. 2c

Fig. 2d

Fig. 2e

Fig. 2 XRD analysis of mixture of potassium silicon fluoride and aluminum (a) original and heated for 1h at (b) 570 °C, (c) 580°C, (d) 600°C and (e) 670°C

According to X-ray diffraction patterns analysis of five different samples (see Fig. 2), the mass percent of aluminofluorides ($KAlF_4$ and K_3AlF_6) and silicon increased with sintering temperature. However, the silicon phase can hardly be identified in X-ray diffraction patterns when the temperature was below 600°C and only a little amount was generated as the temperature increased. So, the formation of silicon phase only causes small thermal effect at 600°C. But, after the melting temperature of Al, the silicon phase was the main phase.

Therefore, it is visible that the phase formation mechanisms are different before and after the melting temperature of Al. To understand the formation process more clearly, detail analysis was implemented at two different stages of solid–solid reaction and solid–liquid reaction below.

3.2.1 Solid–solid reaction stage

From the X-ray diffraction analysis results, it was found that no Si phases formed before 570°C. At the initial stage of the reaction (570°C), only K_2SiF_6 and Al phases were detected (Fig. 2 a and b). There was scarcely any difference between the two X-ray diffraction patterns.

As the sintering temperature increased to 580°C (see Fig. 1, the peak 1), many aluminofluorides ($KAlF_4$ and K_3AlF_6) were formed, fractional silicon phase that can be detected by X-ray diffraction appeared (Fig. 2 c). when the sintering temperature reached 600°C, silicon content slightly increased, aluminofluorides phases was still main phases (Fig. 2 d).

At this stage, silicon phase has no clear increase for the reason that the growth of silicon is restricted by pinning action of pore [10]. On the other hand,

migration-rate of materials is too slow to promote the growth of grain rapidly at this solid–solid reaction stage. Hence, it is hard to form large-scale silicon at this stage.

3.2.2 Solid–liquid reaction stage

when sintering temperature increased to 670°C, the silicon phase was the main phase(see in Fig. 2(e)), which shows that reaction between K_2SiF_6 and Al powders has completed. At this temperature, residual Al melted and the flowing liquid phase (Al) increased the diffusion rate of atom and enlarged the contact area of reactants, which

leads to a strong and complete reaction. This reaction may be written as:

According to the structural theory of slag [11], both $KAlF_4$ and K_3AlF_6 in their molten state may be regarded as molten mixtures of KF and AlF_3 . Therefore, Reaction (1) can be rewritten as:

From the KF- AlF_3 phase diagram in Fig. 3 [12], it can be seen that the binary salt system of KF- AlF_3 at a ratio of 3:2 is located in the range where $KAlF_4$ and K_3AlF_6 are the phases present at room temperature.

Fig. 3 Phase diagram of KF- AlF_3 binary system [12]

4 Conclusion

The formation of silicon is investigated by DSC, and the mechanism is explored by a series of sintering experiments with the aid of X-ray diffraction analysis and sintering theories. It is found out that:

(1) The Si phase starts to form at 580°C, but does not complete until the sintering temperature exceeds 660°C (the melting point of pure aluminum).

(2) Two different forming stages of Si phase are identified: one is the solid–solid reaction stage between K_2SiF_6 and Al powders, which generates a small amount of silicon. The other is the solid–liquid reaction stage, in which the molten Al promotes the reaction between K_2SiF_6 and Al powders.

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