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CHEMICAL REACTION AT HIGH TEMPERATURE AND HIGH PRESSURE VII

Solid State Reaction of Silicon with Graphite to Form Silicon Carbide and Its Stability

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The yield of SiC in the solid state reaction between Si and graphite powder has been studied at temperatures of 800∼1,100°C under pressures of 10∼50 kb. The temperature of commencement of reaction is represented by $0.7 \times T_m$°K (melting point of Si under pressure). The yield of SiC increases with increasing temperature and pressure, so that the rate determining step would be in the reaction process.

The $\alpha \rightarrow \beta$ transformation of SiC has been observed under pressure and it has been concluded thermodynamically that the β form SiC would be the stable species in the experimental conditions.

Introduction

Silicon carbide is prepared by the method of decomposition reaction in vapour phase of silicon compound and hydrocarbon, or the reaction of graphite powder in molten silicon. The crystal structure of silicon carbide, prepared below 2,000°C by a method, is β form (fcc) and it transforms from β to α form (hexagonal) above 2,100°C[1].

Now, the molecular volume of silicon carbide is smaller by about 4.7 cc than the sum of atomic volumes of silicon and graphite, so that the rate of the formation reaction in solid state of silicon carbide may be accelerated under high pressure.

Bundy[2] and Kennedy[3] elucidated that the melting temperature of silicon decreases under high pressure with the rate of about 50°K/10 kb. The decrease of the melting point with pressure would affect the temperature of the commencement of reaction and the yield of reaction.

As mentioned above, the β form of silicon carbide transforms to α form at atmospheric pressure above 2,100°C and the α form is quenched at room temperature so that the transformation is not reversible. Other experiments showed the crystal growth of α form in the temperature range of 1,400∼1,600°C[4]. M. I. Sokhor *et al.*[5] have reported the $\alpha \rightarrow \beta$ transformation under high temperature and high pressure, but the experiments of E. D. Whitney *et al.*[6] have recently shown that the α-SiC

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is favoured by high pressures in the absence of solid solution phases such as boron nitride.

From these points of view, the solid state reaction of silicon and graphite and the $\alpha \rightarrow \beta$ transformation have been examined under high temperature and high pressure.

Experimentals

The powder of each extra pure reactant was of a size in 300 mesh and mixed thoroughly in atomic ratio of Si : C=1 : 1. The reaction product was quantitatively analysed by means of the internal standard in the powder diffraction of x-ray. The reaction yield was determined by the ratio of the intensity of (111) peak of SiC and that of (111) peak of unreacted Si.

In the case of the study of the $\alpha \rightarrow \beta$ transformation of SiC, the reagent grade α-SiC was purified by the dissolution of Si, SiO_2 and others with the mixed acid of HF and HNO_3 and then the ignition of graphite in oxygen atmosphere. The purified sample was confirmed to be the α form only by x-ray analysis. After the compression of the sample at high temperature for 60~120 minutes, the sample was quenched at room temperature under high pressure and then the pressure was released. The pulverized sample was analysed by x-ray diffraciton and the $\alpha \rightarrow \beta$ transformation of SiC was observed.

As shown in the previous paper, the sample was compressed in a cylindrical glassy carbon heater inserted in a pyrophyllite cube as a pressure medium by means of a compact cubic anvil apparatus⁷⁾. The reaction temperature was measured with the Pt-PtRh (10%) thermocouple touched on the outer surface of the glassy carbon heater. Pressure was calibrated by the aid of the phase transitions at room temperature of Bi I–II (25.4 kb), Tl II–III (31 kb), Ba II–III (59kb) and Bi V–VI (89kb).

Experimental Results and Considerations

After the reaction under high pressure, the pulverized product was digested with mixed acid of HF and HNO_3 in order to dissolve the unreacted Si and then ignited the unreacted graphite in the oxygen atmosphere. The greenish fine crystals were obtained as a residue, whose crystal structure is assigned to the β form SiC (fcc), though the reaction product at atmospheric pressure below 2,000°C is the mixture of α and β form¹⁾. It may be suggested that the β form would be more stable at high pressure and there is the possibility of the $\alpha \rightarrow \beta$ transformation under high temperature and high pressure.

Fig. 1 shows the reaction yield after 60 minutes at 10, 30 and 50 kb in the temperature range of 800~1,100°C. The reaction yield increases with increasing temperature at each pressure, respectively. As the result of the extrapolation of these lines to the zero yield, these lines intersect the abscissa at 900°C (10 kb), 800°C (30 kb) and 700°C (50 kb), respectively. In other words, these temperatures correspond to those of the commencement of reaction in solid state under high pressure.

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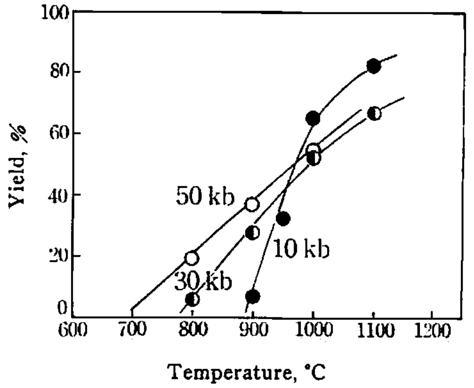

Fig. 1 Variation of reaction yield of SiC with temperature after 60 minutes under high pressures

○ : 50 kb
◐ : 30 kb
● : 10 kb

In Fig. 2, the full line shows the melting temperature (T_m°K) under pressure of Si by Bundy[2] and Kennedy[3] and the dotted line the temperature of the commencement of reaction under pressure that is represented by $0.7T_m$°K. It is noticeable that, in spite of the solid state reaction, the reaction yield after 60 minutes increases with increasing pressure at the definite temperature below 1,000°C, as shown in Fig. 1.

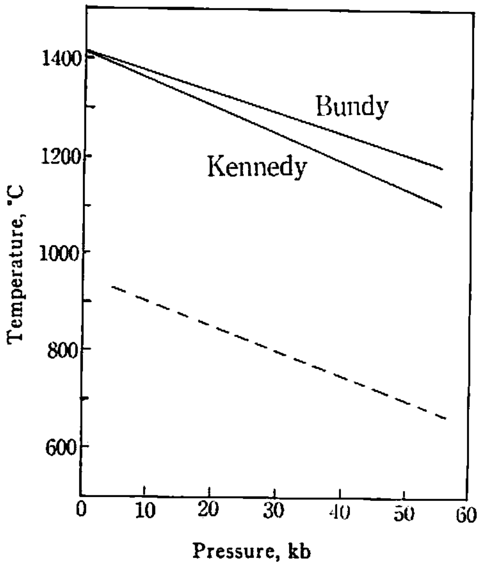

Fig. 2 Variation of melting temperature of SiC and temperature of the commencement of reaction of $Si+C=SiC$ under high pressure

The variations of the reaction yield with the lapse of time are shown in Figs. 3 (a), (b) and (c). At the definite pressure, the yield increases with increasing temperature and with the lapse of reaction time. Though the difficulty of manipulation under high pressure makes the kinetic analysis of experimental data rather complicate, the rate equation of this reaction is best expressed as the second order reaction. In every case, the plot of $x/(1-x) \sim t$ exhibits a straight line and the slopes of these lines give the second order rate constant k as shown in Table 1, where x is the fraction of product at reaction time t.

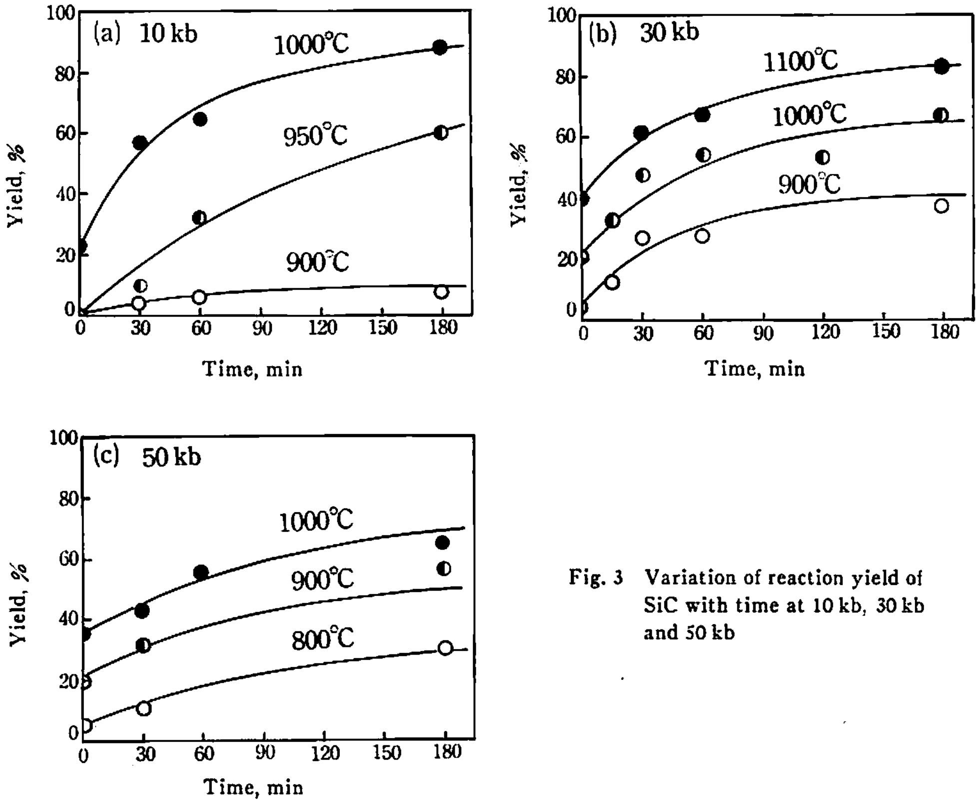

Fig. 3 Variation of reaction yield of SiC with time at 10 kb, 30 kb and 50 kb

Table 1 The second order rate constants in the reaction of $Si+C=SiC$

Pressure, kb	Temperature, °C	$k\times10^3$, min^{-1}
10	900	1.3
10	950	9.3
10	1,000	29.0
30	900	4.8
30	1,000	11.8
30	1,100	25.0
50	800	3.2
50	900	5.8
50	1,000	10.0

The tentative estimation by the Arrhenius plot of k gives 70 kcal/mole at 10 kb, 26 kcal/mole at 30 kb and 15 kcal/mole at 50 kb as the apparent activation energy, respectively, and also -3.6 cc/mole is obtained as the activation volume at 900°C. The remarkable decrease of the apparent acitvation energy with pressure would not be ascribed only to the variation of the thermodynamic condition of the reactants and the activated complex by compression, but the difference of the rate determining step in the reaction process which could not be discussed in this experiment.

The $\alpha \rightarrow \beta$ transformation was examined in the conditions of the temperatures of 400~1,200°C and the pressures of 10~50 kb. Figs. 4(a) and (b) show the x-ray diffraction patterns of α from and

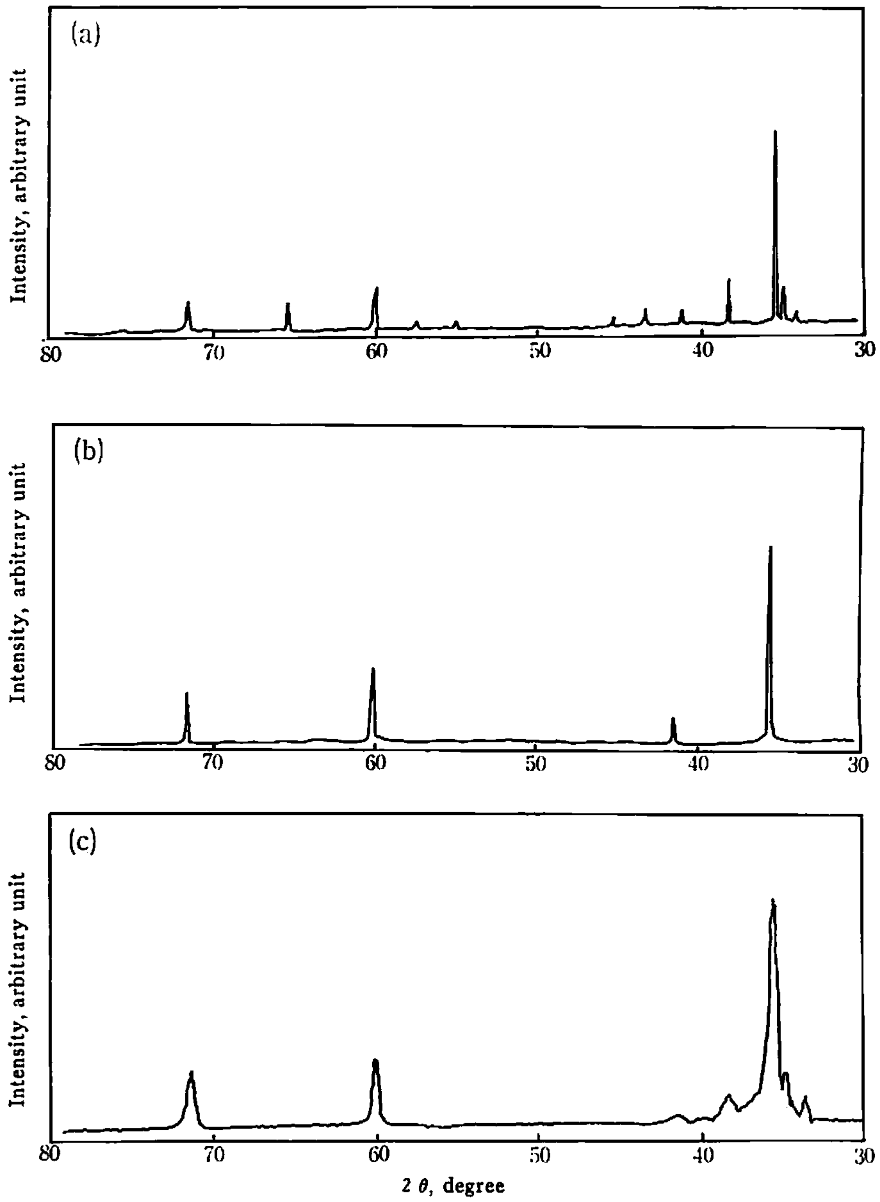

Fig. 4 X-ray diffraction patterns of SiC

(a) : α form

(b) : β form

(c) : after compression of α form at 50 kb, 1,000°C for 120 minutes

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β form, and Fig. 4(c) shows the x-ray diffraction pattern of the sample after compression of 50 kb at 1,000°C for 120 minutes. In Fig. 4(c), the characteristic lines of α form decrease markedly and those of β form are intensified relatively. In general, the characteristic lines of x-ray attributed to α form decrease much more with increasing temperature and pressure, and the rate of the transformation depends on the reaction temperature and pressure. Pressure is more effective in this transformation than temperature as shown in Fig. 5. Fig. 5 shows the boundary of the commencement of the transformation reaction, but not the phase diagram. As the result of this experiment, it is concluded thermodynamically that the β form SiC would be the stable species in this experimental conditions, and the α form SiC the metastable species.

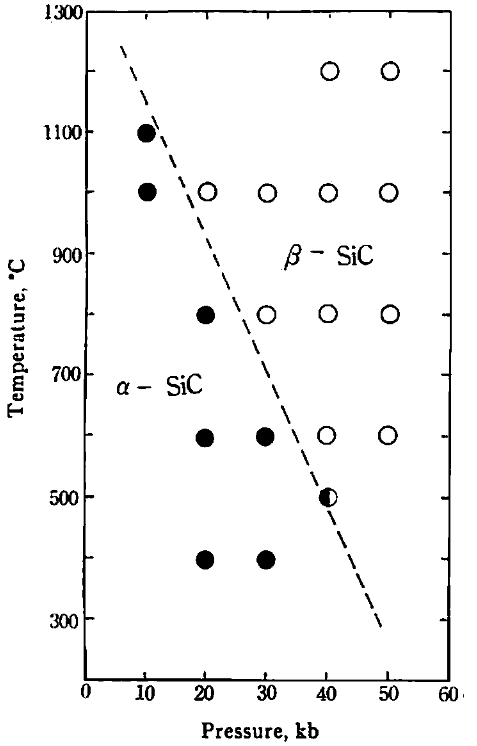

Fig. 5 The boundary of the commencement of the transformation reaction of SiC from α form to β form

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