Melting Behavior of β -SiC at High Pressure

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The melting behavior of β -SiC with diamond structure was investigated under high pressures up to about 10 GPa using a flash-heating device. The peritectic temperature, at which the SiC decomposes into two phases of carbon saturated liquid Si and solid carbon (graphite) by a peritectic reaction, increases with pressure and the formation temperature of one liquid phase (l -SiC) also tends to increase with pressure. The solubility of carbon in liquid Si reach 50% at about 10 GPa and β -SiC melts directly into l -SiC. [silicon carbide, melting temperature, peritectic reaction, carbon solubility, electrical resistivity]

1. Introduction

Silicon and carbon belong to the same group-IV elements, but they have different physical and chemical properties. Liquid silicon (l -Si) shows metallic behavior and a low coordination number of ~ 6.4 [1], lower than those of most liquid metals, ~ 12 . On the other hand, liquid carbon (l -C) is poorly conducting metal [2] and has a very low coordination number of ~ 2.8 , even lower than graphite [3]. Although the melting temperature of Si with diamond structure decreases with increasing pressure, at high pressure l -C is less dense than diamond, indicating a positive slope of the diamond melting line in the phase diagram [4]. This difference raises interesting question about the nature of the liquid state of silicon carbide (SiC), which is an alloy of these two elements with above competing phenomena.

On the other hand the crystalline SiC exists in two allotropic forms, α (hexagonal form with many polytypes) and β (cubic form). As has been shown in an equilibrium phase diagram for Si-C system at 1 atm [5], SiC decomposes by the peritectic reaction into solid C (graphite) and liquid silicon saturated by carbon, l -Si(C), at the peritectic temperature of 2540°C and then converts to one liquid phase (l -SiC) at about 3000°C. However, some discrepancies still remain concerning the peritectic temperature and the liquidus composition [6, 7] as well as the thermodynamical stability of α - and β -SiC.

The purpose of this paper is to investigate the melting behavior of β -SiC (3C-SiC) with diamond structure in connection with the p - T phase diagram of SiC.

2. Experimental

Sintered polycrystalline β -SiC (99.4 w% in purity, including 0.08w% free C, lattice constant of $a_0 = 0.43588 \pm 0.00008$ nm) was used as specimen. The experiments were carried out in the pressure range of 2.4 to 9.4 GPa using a 6-8 anvil type high pressure apparatus. The sample was a

semiconductor with low resistivity and directly heated by the discharged current of capacitor bank (flash-heating method) [8]. The heating power W , inserted energy J (integral of electrical power) and resistance R (or resistivity ρ) versus time curves were derived from the voltage drop V across the sample and the circuit current I .

3. Results and Discussion

3.1. Change of Resistivity of SiC by Heating

Figure 1 shows the resistivity change obtained as a function of inserted energy for β -SiC at 5.6 GPa. The curve indicates a typical resistivity change in an impurity semiconductor with increase of temperature (corresponding to inserted energy in

Fig. 1. Resistivity vs. inserted energy curve at 5.6 GPa.

The J_a and J_b show the energies at the start of fusion and $\rho_b = 0.8$ mΩ cm respectively.

the figure); i.e., first the resistivity decreases in the impurity region and increases through a minimum of resistivity due to the decrease of the carrier mobility in the saturation region. In the intrinsic region the resistivity decreases again with further increase of temperature, because of increase of number of conduction electron. In order to verify the start point of fusion of β -SiC in the resistivity data, we examined some samples which were quenched by cutoff of current and recovered at ambient pressure and temperature. The sample, which was quenched at J_a (at ρ_a , the point of inflection on the decreasing resistivity curve) showed almost the same texture as the starting sample. On the other hand the radial texture, which indicates an evidence of solidification from the molten state, was clearly found in the samples quenched at the inserted energy above J_b (the resistivity below $\rho_b = 0.8 \text{ m } \Omega \text{ cm}$). The inserted energy J_b includes the latent heat to the phase change in addition to the energy required to reach the molten state, because the sample already show a radial texture. Although it is difficult to decide the start point of fusion, in this experiment we took the energy J_a , which is that at the point of inflection on the resistivity curve in Fig.1, for the energy required to reach the molten state.

3.2 Change of Inserted Energy J_a with Pressure

Figure 2 shows the summary of the experimental data concerning the energy at the start of fusion J_a , the energy J_b at $\rho_b = 0.8 \text{ m } \Omega \text{ cm}$ and the cut-off energy in the quench experiments. The energy required to reach the fusion state tends to increase with pressure.

Fig. 2. Pressure dependence of the inserted energy of J_a and J_b . The cut-off energy for the quench run and the results of the observation of recovered samples are shown by squares.

3.3 X-ray Data of Samples Recovered from Molten State

Figure 3 shows the X-ray diffraction data of samples recovered after the complete fusion by free discharge at the pressures of 2.5 to 9.4 GPa. It shows that β -SiC crystallizes from the molten state together with graphite and Si, which were produced by the decomposition reaction. The amount of graphite and Si tends to decrease with pressure. If SiC is supposed to be presented from only the carbon saturated I -Si [I -Si(C)] in the cooling process, the solubility of carbon in I -Si could be estimated from the ratio of graphite or Si to SiC. The quantitative analysis of graphite and SiC was undertaken by the intensity ratio of those strongest peaks, G(002) and β (111) respectively, based on the X-ray data in the mixed powder of graphite and SiC with the known ratios.

Fig. 3. X-ray diffractions of the samples recovered from the molten phase after the flash-heating of β -SiC at high pressure.

3.4. Solubility of Carbon in I -Si

The results of X-ray diffractions are summarized in Fig. 4. The solubility of carbon in I -Si increases with pressure above 5.6 GPa and tends to reach 50% at about 10 GPa. This suggests that the peritectic reaction gradually suppresses with increase of pressure and at about 10 GPa solid SiC directly melts into one liquid phase (I -SiC) without any decomposition before the melting. Below 4 GPa the solubility may decrease with pressure and as shown in Fig. 4 the solubility seems to rapidly change between 4 GPa and 5.6 GPa. Although the further experimental study would be required to clarify the pressure dependence of solubility of carbon in I -Si, this

experimental results roughly consistent with 25 at% at 1 atm [5] and 19 at% at 35 atm [6].

Fig.4. Solubility of carbon in *l*-Si. The solubility obtained at low pressure by Dolloff [5] and Scace and Slack [6] are shown by solid hexagon and solid diamond respectively.

3.5. Possible Phase Diagram of SiC

Figure 5 shows a possible *p*-*T* phase diagram of SiC, which is derived from the inserted energy J_a data in Fig. 2 and a consideration concerning the solubility of carbon in *l*-Si in Fig. 4. The inserted energy corrected for the heat loss during the flash-heating was converted to the temperature using the temperature dependence of enthalpy of β -SiC in JANAF thermophysical data. The behaviors of fusion are considered as follows,

- (1) The fusion includes the peritectic reaction by which β -

Fig. 5. Possible phase diagram of SiC at high pressure. The results of Dolloff [5] and Bhaumik et al. [9] are shown by solid hexagon and solid triangle respectively.

- (1) SiC produces *l*-Si saturated by carbon, *l*-Si(C).
- (2) The fusion temperatures for 2.5 and 4 GPa consistent with the peritectic temperatures reported by Dolloff [5] and Bhaumik et al. [9]. This means that the peritectic reaction is possible to occur during the rapid heating in this pressure region.
- (3) The solubility data in Fig. 4 suggests that at about 10 GPa β -SiC directly transforms to *l*-Si with 50% solubility of carbon, namely *l*-SiC. The fusion (melting) temperature is about 3300°C. If we use the formation temperature of *l*-SiC, about 3000°C at 1 atm, suggested by Dolloff [5], the liquidus line could be described by a line with a positive slope as shown in Fig. 5. The fusion temperature of 5.6 and 7.4 GPa also is those in the transformation of β -SiC to *l*-SiC and in this pressure region *l*-SiC may be able to be directly brought from β -SiC during the rapid heating.
- (4) The solidus line, which means the peritectic reaction of β -SiC with increase of temperature, has a positive slope. At about 10 GPa the line is cross to the liquidus line which shows the formation of *l*-SiC.
- (5) The β -SiC is a low temperature and high pressure stable phase [10] and the equilibrium line between α - and β -SiC [10] is interrupted by the solidus line. The stable *p*-*T* field of α -SiC may be very small.

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