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Author(s)	Yoshikawa, T; Kawanishi, S; Tanaka, T
Citation	Journal of Physics: Conference Series. 165(1) P.012022
Issue Date	2009
Text Version	publisher
URL	http://hdl.handle.net/11094/25983
DOI	info.doi/10.1088/1742-6596/165/1/012022
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2009 J. Phys.: Conf. Ser. 165 012022

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Fundamental study for solvent growth of silicon carbide utilizing Fe-Si melt

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Abstract. Fe-Si melt is a candidate for use as an alloy solvent for rapid liquid phase growth of SiC because of the high solubility of carbon in molten iron. In this work, the equilibrium phase relationship between SiC and the liquid phase of the Fe-Si-C system was investigated at 1523 K by the phase equilibration technique, and was further studied with the thermodynamic calculation. It was found that Fe- 36 mol% Si melt equilibrates with SiC at the temperature and possesses the higher carbon solubility than silicon-based melt. The first trial of the SiC crystal growth experiment was then carried out with Fe- 36 mol% Si melt by means of temperature difference method, and formation of SiC layer was obtained on the graphite substrate. Accordingly, it was found possibility for rapid growth of SiC by the solvent growth method with Fe- 36 mol% Si melt.

1. Introduction

Silicon carbide (SiC) has attracted attention as a basic semiconductor material for high temperature electronics and high power switching devices due to its wide bandgap, high electrical breakdown field and high thermal conductivity. Physical vapor deposition (PVD) is the standard method for the production of a bulk SiC single crystal, but it requires the controlled operation for SiC sublimation above 2200 K. The development of a low cost method for SiC material production is thus essential before wide-scale use of SiC semiconductor. We have focused on the liquid phase growth technique for the low temperature production of SiC.

Regarding to the liquid phase growth method of SiC, several research have been conducted using silicon-based alloy solvents such as silicon, Si-Ge or Si-Ti melts at above 1780 K, aiming for epitaxial growth on a SiC substrate [1 - 3]. Although epitaxial growth was achieved, the growth rate was not as high as that in the PVD method. This may be caused by the low solubility of carbon in the silicon-based solvent which accounts 80 ppmw at 1800 K in molten silicon [4]. We have applied the iron-based solvent containing silicon because of the high solubility of carbon in molten iron. The low eutectic temperatures of the Fe-Si system of around 1500 K can be effectively used for liquid phase growth at lower temperatures than has been done previously [1 - 3].

For the liquid phase growth of SiC using Fe-Si solvent, the phase diagram for the Fe-Si-C system is indispensable for determining the solvent composition. Investigation on the phase equilibrium in the Fe-Si-C system, however, is limited in the iron-rich corner and only a literature dealing with the liquid phase region saturated with SiC is available [5].

Therefore, the equilibrium phase relationship between SiC and the liquid phase in the Fe-Si-C ternary system was investigated in the present work. It was measured by an equilibration technique

and was also estimated using thermodynamic calculation at 1523 K. Fe- 36 mol% Si alloy was found to be in equilibrium with SiC at the temperature. Furthermore, the growth experiment of SiC using the Fe-36 mol% Si solvent was carried out at 1523 K by means of temperature difference method. Formation of the SiC layer was obtained on the graphite substrate and the applicability of the alloy was clarified as the solvent for the liquid phase growth of SiC.

2. Equilibrium phase relationship between SiC and Fe-Si melt

Phase relationship between SiC and Fe-Si melt was only reported by Chipman et al. [5]. It was shown that the liquid composition in equilibrium with both SiC and graphite was Fe- 33.2 mol% Si at 1473 K and increased the Si content to Fe-37.7 mol% Si by increasing temperature to 1963 K. Here, the phase equilibrium between SiC and Fe-Si melt and the solubility of carbon in the melt was investigated around the liquid composition of Fe- 35 mol% Si.

Experiments were carried out with a vertical SiC resistance furnace. Fe-30, 33 and 36 mol% Si alloys were prepared by melting high purity electrolytic iron (99.992 %) and semiconductor-grade polycrystalline silicon (12N) in an alumina crucible at 1733 K under an argon atmosphere and then quenched in water. Five grams of Fe-Si alloy together with a dense graphite tablet or a SiC compact were inserted into an alumina Tammann tube (ϕ 12mm) and kept in a furnace at 1523 K for 16 or 24 hours under an argon atmosphere. SiC compacts were prepared by the following methods: Equimolar mixture of 5N silicon and 3N carbon powder was compressed to form a disk at 50 MPa and then subjected to reactive liquid phase sintering by induction heating or spark plasma sintering (SPS) at temperatures higher than 1723 K under vacuum. Carbon analysis of the alloy was carried out by the combustion-IR absorption method. Silicon content was determined by SiO₂ gravimetric analysis or ICP atomic emission spectrometry.

Experimental results for the equilibrium composition of Fe-Si alloys saturated with SiC or graphite are shown in Fig. 1. The Fe-36 mol% Si alloy was in contact with SiC when the alloy was kept with either a graphite disk or a SiC compact, whereas no SiC layers were seen in the Fe-30 and 33 mol% Si alloys. The liquid composition in equilibrium with both graphite and SiC thus exists between 33 – 36 mol% Si at 1523 K. Chipman et al. [5] also reported comparable silicon content for that composition even though the carbon content seemed to be slightly lower than the content here.

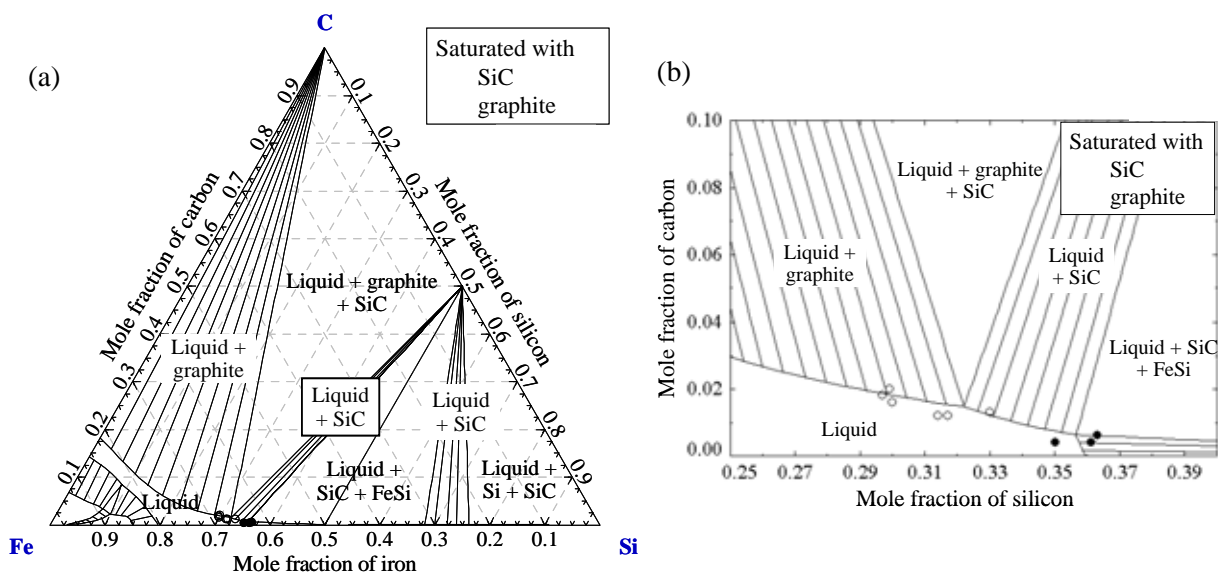


Figure 1 Experimental results for the equilibrium phase relation of Fe-30 – 36 mol% Si with the corresponding solid phase at 1523 K together with calculated results. (a) entire isothermal section of the Fe-Si-C system and (b) partial section.

The equilibrium phase relationship between SiC and the liquid phase in the Fe-Si-C system is further evaluated by thermodynamic calculations. The excess molar Gibbs energy in the liquid phase is described by a Redlich-Kister type polynomial given by Eqs. (1) and (2). Contributions of the binary Fe-Si, Fe-C and Si-C systems are taken into account here.

$$\Delta G_{m,liq}^{Ex} = x_{Fe}x_{Si}L_{Fe-Si,liq} + x_{Fe}x_C L_{Fe-C,liq} + x_{Si}x_C L_{Si-C,liq} \quad (1)$$

$$L_{i-j,liq} = \sum_{m=0}^n \{ {}^m L_{i-j,liq}(T) (x_i - x_j)^m \} \quad (2)$$

where $L_{i-j, liq}$ represents an interaction parameter between components i and j in the liquid phase and was referred to the literature [6-8]. The equilibrium calculation was carried out with thermodynamic calculation software (FactSage 5. 5). The calculated results of the isothermal section of the Fe-Si-C system are shown in Fig. 1 (a) and (b). A good agreement was obtained between experiments and calculations. The validity of the estimated equilibrium relationship of the iron-rich liquid phase saturated with SiC in the Fe-Si-C system was thus confirmed.

To optimize the Fe-Si solvent for rapid crystal growth of SiC, composition dependence of carbon solubility in Fe-Si melt was calculated as shown in Fig. 2. The solubility of carbon in iron-rich Fe-Si alloy was found to be 100 times higher than that in silicon-rich alloy. Hence, the Fe-Si melt of Fe-36 mol% Si composition which possesses high carbon solubility is expected to be a suitable solvent for rapid liquid phase growth of SiC.

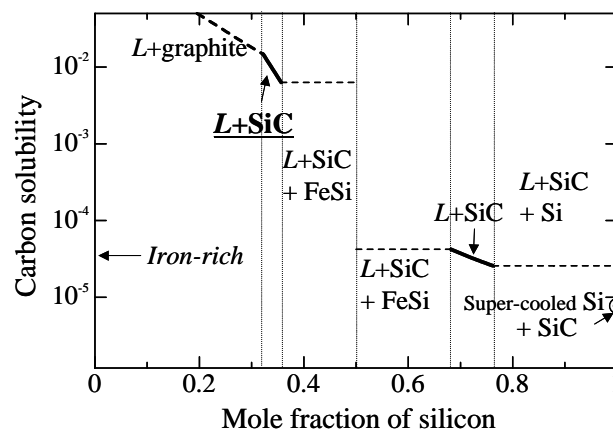


Figure 2 Calculated composition dependence of carbon solubility of the Fe-Si melt at 1523 K.

3. Trial of the liquid phase growth of SiC with Fe- Si solvent

First trial of the liquid phase growth of SiC with Fe- Si solvent was conducted by means of temperature difference method. The Fe-Si alloy is put between two graphite substrates and is placed in the temperature gradient. The difference in the carbon content at two interfaces between the alloy and graphite substrates brings mass transfer of carbon from high to low temperature interface, resulting in continuous dissolution of graphite and precipitation of SiC at high and low temperature interfaces, respectively.

The Fe- 36 mol% Si alloy prepared by the above-mentioned method was cut and polished to the square plate ($5 \times 5 \times$ about 1 mm). The alloy was sandwiched between two graphite substrates and was suspended in the temperature gradient region in a vertical SiC resistance furnace at 1523 K under an argon atmosphere and kept for 16 h. Experiment was carried out with the different temperature gradients of 14 and 21 K / cm.

The cross sections around the graphite substrate at low temperature interface are shown in Fig. 3. Since the grown layers of SiC were observed on graphite substrates, the applicability of the Fe-Si alloy as a solvent for the liquid phase growth of silicon carbide was clarified. Further, temperature gradient

affects the thickness of the grown layer, which indicates that its growth kinetics is at least partly limited by the mass transfer in the solvent. In future, the authors will try rapid growth of SiC by enhancing the forced convection in the solvent.

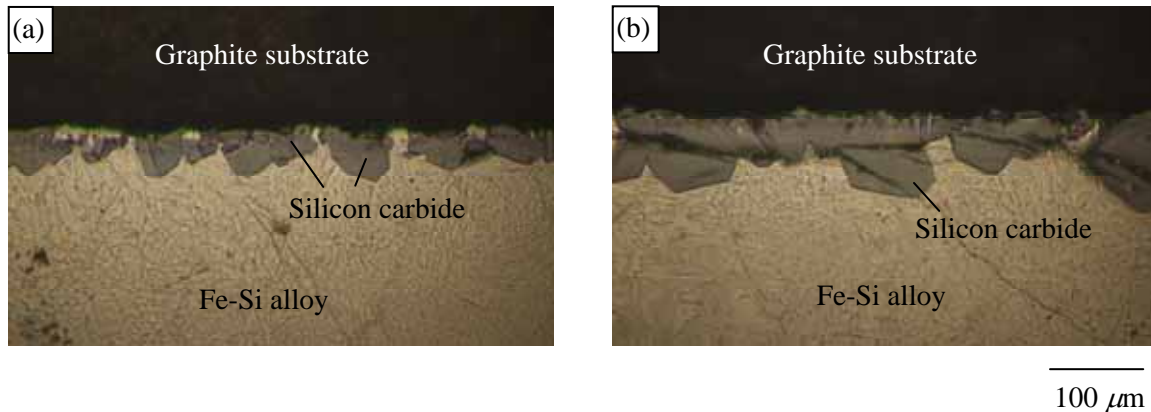


Figure 3 Microstructures around the low temperature interface between Fe-Si alloy and a graphite substrate after holding at 1523 K for 16 h. Temperature gradient; (a) 14 K / cm and (b) 21 K / cm.

4. Conclusion

In order to use Fe-Si melt as a solvent for rapid liquid phase growth of SiC, the fundamental study was carried out in the present work. The equilibrium composition of the Fe-Si melt with SiC was investigated at 1523 K by the equilibration of the Fe-Si melt with SiC or graphite. It was also studied with the thermodynamic calculation. Fe- 36 mol% Si melt was found to equilibrate with SiC at the temperature and possess the higher carbon solubility than silicon-based melt. The SiC crystal growth experiment was then carried out with Fe- 36mol%Si solvent by temperature difference method, and the formation of SiC layer was observed on the growth substrate of graphite. Accordingly, it was found possibility for rapid growth of SiC by the solvent growth method with Fe- 36 mol% Si melt.

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Acknowledgement

This research is partly supported by a Grant-in-Aid for Young Scientists (Start-up) and Priority Assistance for the Formation of Worldwide Renowned Centers of Research - The Global COE Program (Project: Center of Excellence for Advanced Structural and Functional Materials Design) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.