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Examination of the interaction between liquid silicon and bulk silicon carbide



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ABSTRACT

Little information is available about the evolution of SiC in the presence of molten silicon. In this context, two kinds of experiments relative to the interaction between SiC substrates and molten Si were performed between 1450 and 1600 °C with: (1) dense α -SiC bars and (2) dense α -SiC pellets coated with a β -SiC layer deposited by CVD. The results obtained indicate that an important crystal growth occurs in any cases. Large and faceted SiC crystals have grown on the surface of the SiC substrates and on the whole surface of molten silicon. These crystals are formed by dissolution-growth mechanism of SiC substrates with kinetics depending on the temperature. Low thermal gradients within the samples and between the inner parts and/or the surface of the samples could noticeably promote the evolution of the system by generating a carbon flux. The interaction between molten silicon and SiC is of importance because it could have some effects on the physical and chemical properties of the materials. It is well known that large grains are deleterious for mechanical properties.

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1. Introduction

SiC has a fairly large ionicity value of 0.177 on the Phillips scale (Garcia-Cohen 0.475 and Pauling 0.11) [1]. Nevertheless, SiC is generally considered as a covalent bonded compound (88% covalency and 12% ionic), what is sufficient in most cases to explain its chemical properties. This compound is of great importance in a broad range of technological applications because of its wide band gap, good oxidation resistance, high thermal conductivity, low density, high stiffness and adequate toughness. However, a complete understanding of the chemical behavior of this compound during the elaboration and utilization stages of the SiC-containing materials is essential. As shown in Fig. 1, the Si–C system calculated with ThermoCalc software contains only SiC as binary compound [2,3]. Consequently, this phase can be synthesized easily by a reaction between silicon and carbon. In this way, many studies deal about the synthesis of SiC by using different processes. The general idea is to promote the wetting and the reaction between molten silicon and carbon in order to form SiC [4–13]. The synthesis of composites materials for high temperature applications by reactive infiltration of silicon in carbon-filled preform is also a promising application of this system [14–17]. Nevertheless, according to the results in the literature, the interaction between the liquid phase and carbon is complex and not fully

mastered. In a general manner, the reaction between silicon or containing-silicon alloys and carbon is known to be sudden, strongly exothermic and generally uncompleted with remaining carbon and/or free silicon [5,6,13,18]. The interaction between the liquid and the as-formed SiC is also important because it could have some effects on the properties of the so-obtained material. The effects on the microstructure of the interaction between a liquid and a ceramic were discussed by Lee et al. [19]. In this way, it was demonstrated that the presence of a low quantity of liquid during the SiC sintering at 1970 °C for 6 h is able to control the grain growth kinetic and the microstructure during the transformation of β -SiC to α -SiC by dissolution–reprecipitation with core/rim microstructure [20]. It is worth noting that SiC is known under several polytypic forms [21]. Up to now, the interaction of SiC with molten alloys was extensively examined from the perspective of the wetting and of the reactivity in metal/ceramic couples for technological processes but there is only few information about the reactivity of pure molten silicon with SiC substrate [22–25]. A study on the dissolution morphology of SiC wafers in contact with molten Fe–Si alloy at 1300 °C indicates that the dissolution kinetics could be limited not only by the mass transfer but also by the interfacial reaction [26]. Narumi et al. also demonstrated on the basis of thermodynamic calculations that the addition of metallic elements as chromium, iron or titanium can accelerate SiC growth by increasing carbon solubility in the melt [27]. In the same way, it was reported that the contact between α -SiC and Si₂₅Ge₇₅ melts between 1100 and 1400 °C leads to the formation of β -SiC islands, first on the substrate and later on the carbon

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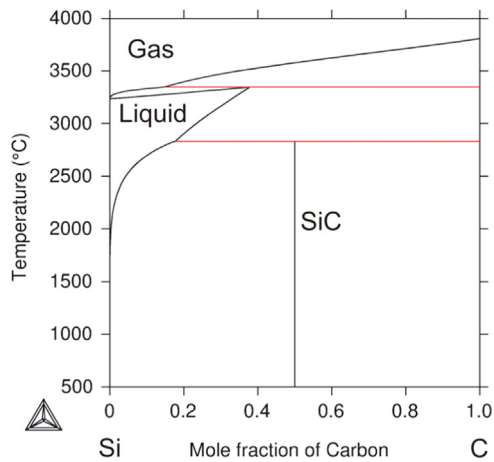


Fig. 1. Calculated Si–C diagram [2,3].

crucible by dissolution and transport of carbon [28]. Thus, the influence of the substrate polytype, the temperature, the heating rate and duration was demonstrated on the transformation of the SiC substrates. One also knows that the contact angle of pure molten silicon or of the alloys Cu-25at% Si and Ni-40at% Si on α -SiC depends on the polar surfaces of the substrate [24]. The contact angle on the (0001)-SiC polar surface is the lowest in any cases and it is reduced by the use of an alloy which promotes adhesion. α -SiC and β -SiC differ only from the ninth structural layer. These two kinds of SiC were examined because of the possible occurrence of a preferential dissolution along some crystallographic planes. Despite the high similarity of the α - and β -SiC polytypes, their crystallographic structures are not exactly the same, one having a cubic lattice and the other one a hexagonal lattice. The α -variety is stable at high temperature, above 2000 °C, and the β -variety is formed at lower temperatures. The chemical stabilities of these phases are a little different. The solubility and the diffusion coefficient of carbon in liquid silicon are determinant characteristics. That is why they were examined at 1600 °C by Eremenko et al. [29]. Some other authors also examined the solubility of carbon in molten silicon [3,30–33]. It is clear that carbon is very slightly soluble in molten silicon at 1450 °C (less than 100 ppm in mass) but all the studies indicate a noticeable increase with temperature (Fig. 2). The aim of the present work is to obtain more details about the dissolution and growth phenomena of SiC in molten silicon between 1450 and 1600 °C. With this aim, experiments have been done to identify the reaction mechanisms and the conditions promoting the reaction. Two kinds of substrate were examined: α -SiC with large grains and 3% of porosity and dense β -SiC with smaller grains.

2. Materials and experimental procedures

The Si powder (99.995 wt% Si, grade AX-20, Starck, Germany) used in these experiments has a mean particle size of 7.5 μm . Bulk SiC was purchased from Boostec Company, France. It is composed of dense α -SiC obtained by sintering at 2000 °C with a low residual porosity less than 3% with a mean grain size of 5 μm . The interaction between massive SiC and molten Si was examined via a set of four experiments at 1450 and 1600 °C for the duration of 4 h in alumina crucibles ($\varnothing 15 \times 30 \text{ mm}^3$) coated with pure micronic boron nitride (BN) deposited from a suspension which is used as a protective layer (Fig. 3). Indeed, the BN coating has the advantages of being non-reactive and poorly wettable with respect to the molten silicon, thereby preventing the reaction between the

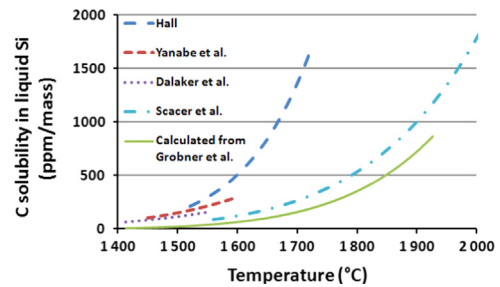


Fig. 2. Solubility of carbon in molten silicon from literature [3,30–33]. The values from Grobner et al. were calculated by using ThermoCalc software [2].

molten silicon and the crucible. The smallness of the samples was chosen to minimize the thermal gradients that are estimated to be lower than 3 °C. In a first case, two bars of bulk SiC ($5 \times 5 \times 25 \text{ mm}^3$), with surface polished down to 1 μm , were each placed in crucibles with 5 g of Si powder and heated at 1450 for one and 1600 °C for the other one. In the second case, two pellets of dense SiC ($\varnothing 8 \times 3 \text{ mm}^3$) coated by a β -SiC layer with a mean thickness estimated to 6.50 μm and a mean grain size of about 1 μm were also placed at the bottom of the crucibles in contact with the BN coating and heated with 5 g of Si powder at 1450 for one and 1600 °C for the other one. The β -SiC layer was obtained by Chemical Vapor Deposition (CVD) at 1000 °C from a mixture made of methyltrichlorosilane and dihydrogen [34]. In all cases, the heating was performed in an inductively heated graphite susceptor in the presence of hafnium powder as oxygen getter. During the temperature increase, a deoxidization step of the materials was made by maintaining the temperature at 1395 °C, below the melting point of silicon, during 1 h under a dynamic vacuum with a pressure of 5.10^{-7} bar. Then, a continuous flow of high purity argon under normal pressure was applied to prevent silicon vaporization and oxygen pollution. After heating, the samples were cut in order to examine the interaction surfaces between the bulk SiC and the liquid. The micrographic observations were performed with a FEI Quanta 400 FEG scanning electron microscope, and the chemical compositions were analyzed by EDX (EDAX Genesis XM4), operated at 10 kV.

3. Results

According to the Si–C phase diagram, SiC and carbon-free molten silicon are not in equilibrium (Fig. 1). The first interaction that occurs is the carbon saturation of the liquid by dissolution of SiC. The solubility of carbon in molten silicon between 1450 and 1600 °C being low (Fig. 2), a much reduced quantity of SiC is dissolved to saturate the liquid. The mass of SiC decomposed to saturate 5 g of pure silicon at 1600 °C is estimated to be about 1.10^{-3} g. So, it could be considered as negligible.

3.1. Interaction between molten silicon and the atmosphere of the furnace

Prior to the examination of the SiC–Si interaction, the melt of 5 g of pure silicon was realized at 1600 °C for 4 h in alumina crucible coated with BN. One can see in Fig. 4 that a continuous layer of SiC crystals with a thickness between 25 and 50 μm has been formed on the surface of the melted silicon with some protuberances enriched in SiC crystals. It can be deduced that during the heating, the atmosphere of the furnace contains traces of molecules promoting the transportation of carbon from the graphite susceptor. This leads to the nucleation and growth of SiC crystals at the triple point of the system which is the surface of the

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