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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 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.

Keywords: A1. Diffusion; A1. Recrystallization; A2. Growth from melt; A2. Natural crystal growth; B1. Inorganic compounds; B2. Semiconducting silicon compounds;

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 on Figure 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. On 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. On 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 W.E. Lee et al. [19]. On this way, it was demonstrated that the presence of a low quantity of liquid during the SiC sintering at 1970°C for 6 hours is able to control the grain growth kinetic and the microstructure during the transformation of β -SiC to α -SiC by dissolution-precipitation 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]. T. 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]. On the same way, it was reported that the contact between α -SiC with Si₂₅Ge₇₅ melts between 1100 and 1400°C leads to the formation of β -SiC islands, first on the substrate and later on the carbon 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-25%at.Si and Ni-40%at.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 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 V.N. Eremenko et al. [29]. Some others authors examined also 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. In 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 to 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 were examined via a set of four experiments at 1450 and 1600°C for duration of 4 hours 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 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 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 hour 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 hours in alumina crucible coated with BN. One can see on the Figure 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 melt in the present case. The so-obtained SiC layer can generate a passivation effect with a very low later evolution of the layer.

3.2 Interaction between SiC bars and molten silicon

The first set of two samples examined was composed of a bar of sintered α -SiC partially surrounded by 5 g of silicon, as represented on the Figure 3-a. After the heating at 1450 or 1600°C, the samples exhibit significant differences as shown on the Figures 5 and 6. In both cases, SiC crystals are formed at the surface of the melt, a stronger quantity is obtained at 1600°C (Fig. 5-a, Fig. 6-b). As showed on the Figure 5-b, large crystals of SiC are formed at 1450°C on one corner of the bar. A closed examination of the SiC-Si interfaces (Fig.5-c) brings to the light that the sizes of the crystals are comprised between 10 to 100 μm and most of them are smaller than 50 μm and grew from the surface of the SiC substrate. The bigger ones, larger than 50 μm , are close to the substrate surface but generally without bonding. The other side of this sample is crystal-free and seems to have been locally attacked and weakened by the liquid (Fig. 5-d). The situation is a little different with the SiC bar heated at 1600°C (Fig. 6). Indeed, the SiC layer at the surface of the melt is continuous and thicker, what could be attributed to the higher temperature. One can also observe that the liquid covers a large part of the SiC bar and wets the top of the sample; this was not the case for the sample heated at 1450°C. The liquid which covers the not-immersed surfaces contains a great quantity of SiC crystals forming some kind of parallel layers along the surface of the substrate (Fig. 6-a). On the upper part of the immerge surfaces, a continuous and free layer made of large SiC crystals was formed (Fig. 6-b). On the bottom part of the substrate, only few small crystals grew locally without forming a continuous layer (Fig. 6-c,d). From these results it can be deduced that two phenomenon occur during the heating leading both to the growth of large SiC crystals. At relative low temperature i.e. 1450°C, a dissolution-growth process occurs but it is controlled by a thermal gradient through the sample. The estimation of the dissolution rate of

the SiC was difficult to realize because it was needed to keep intact a part of the starting surface of the substrate close to the melt. Measurement attempts were not significant due to insufficient thickness variations. The dissolution area is believed to be elevated compared to the area of growth, so that the quantity of SiC dissolved is too few to be precisely measured. Indeed, as schematically represented on the Figure 7, the bottom of the sample (crucible, SiC bar and molten silicon) is in contact with the susceptor and its top part is in direct contact with the Ar atmosphere of the furnace inducing a cooling effect. As a consequence, the dissolution occurs on the whole surface of the substrate but in a more consequent proportion at the hotter side. The large SiC crystals are then formed at the colder side. The tilt of the sample heat treated at 1450°C leads to the growth of the SiC crystals on one side of the bar, the most cooled by the gas flow, detrimentally to the other side. At 1600°C, the crystal growth is promoted and it is believed that a continuous layer of large SiC crystals was formed and grew on the colder surfaces of the bar. When a given size of the layer is reached, it becomes unstable and come apart from the substrate (Fig. 6-b). This is induced by the growth of a layer that occurs only from some crystals at the surface of the substrate, as shown on Figure 5-c. Attentively watching Figure 6-a, it can be observed than the layer at the surface of the substrate is not adherent and is about to breaking away. This instability is induced by the growth of SiC crystals between the layer and the substrate and maybe also by the partial dissolution of the substrate. It must be specified for more comprehension that the corresponding sample being less tilted, the colder surfaces were located symmetrically along the bar so that the growth of the SiC crystals occurs on the whole upper side of the bar detrimentally to the lower side. This behavior tends to suggest that the SiC layers grow from the colder surface of the substrate up to become free. The liquid that wets the non-immersed surfaces of the sample (Fig. 6-a) exhibits a clear sequence of successive SiC layers which could be promoted by carbon supply by the atmosphere, the exchange being facilitated by a relative large surface of exchange. It should be noticed that if the formation of SiC crystals was only induced by the carbon from the furnace atmosphere, the formed layer should be

more adherent on the substrate. This property is the basis of the epitaxial or heteroepitaxial growth of SiC layers by Vapor-Liquid-Solid (VLS) mechanism [35-37]. This process probably occurs but it is not believed to be dominant.

3.3 Interaction between SiC pellets coated with β -CVD SiC and molten silicon

The second kind of samples used in this work is made of dense α -SiC pellets coated by a β -SiC layer (Fig. 8, 9). These pellets were placed in contact with molten silicon in order to cover the whole surface. This configuration is different from the previous samples by the facts that the SiC at the surface is β -SiC and that the samples are smaller. In the case of the sample heated at 1450°C for 4 hours, large crystals of about 50 μm grow on a large part of the pellet surface (Fig. 8-b). The β -SiC coat close to the large SiC crystals was found similar or a little reduced (Fig. 8-c), the mean thickness on 20 measures being estimated equal to 6.30 μm comparing to the initial thickness of 6.50 μm . But some others surfaces were crystals-free and the β -SiC layer was found sensibly more attacked with an average thickness estimated on 20 measures equal to 6.10 μm (Fig. 8-d). So, the thickness loss is weak depending on the considered area. Nevertheless, this lost of matter seems sufficient to generate some thick crystals on one side of the sample. Once again, the influence of thermal gradient through the sample could induce a preferential area of growth of the crystals detrimentally to the hottest part of the surface. For the sample heated at 1600°C, it was found that the whole surface of the melt is covered by a continuous SiC layer. The quantity of SiC crystal formed at the top of the Si melt, above the pellet, is also higher and generate some large protuberances as show on the Figure 9-a. The formation of some crystals is also observed at the top and on the sides of the pellet (Fig. 9-b,c). An infiltration of liquid inside the pellet also occurs but only on the upper part (Fig. 9-b). Moreover, the surface of the SiC pellet is strongly attacked with the total dissolution of the SiC layer formed by CVD. The decomposition of the SiC layer is still in progress at the bottom of the pellet close to the interface between the liquid and the area

protected by the BN coating (Fig. 9-d). From these results, the dissolution of SiC is found very important on the whole surface in contact with molten silicon up to destroy the β -SiC layer. It is worth noting that only few isolated crystals were found into the melt of silicon. One can consider that at least two stages occurred; the first one is the dissolution-growth of SiC close to the surface of the pellet. The second stage is the growth of many crystals at the surface of the melt to the detriment of the crystals grown at the surface of the pellet. This last fact is induced by the thermal gradient through the melt cooled by the argon flow, the upper part being colder than the lower one.

4. Discussion

The Figure 7 summarizes schematically the results obtained after the heating of the SiC bulk samples at 1450 and 1600°C during 4 hours. All the observations demonstrated that a noticeable interaction occurs between dense SiC and molten silicon. A mechanism is proposed on the Figure 10. In a first stage, a (Si,C) liquid saturated in carbon is formed by the dissolution of a small amount of dense SiC and/or by the supply of carbon from the furnace atmosphere. Then, the dissolution-growth occurs first by the dissolution of SiC in the liquid mainly on the hottest surface of the substrate with the growth of some favorable crystals on the coldest side by carbon transportation through the liquid. But, the precipitation and growth of large crystals occur also at the top surface of the melt by carbon transportation from the graphite susceptor. The development of these SiC crystals can form a continuous layer at the surface of the melt generating a new and colder substrate which interferes with the dissolution-growth of SiC crystals at the surface of the substrate by catching more and more carbon from the substrate and from the grown crystals. The competition between the different areas depends on their temperature and consequently on their carbon solubility. Indeed, the hottest liquid areas having higher carbon solubilities, the chemical homogenization of the liquid by diffusion of carbon enriches the coldest areas up to supersaturation inducing the growth of the closest crystals. This mechanism provokes the dissolution of the large SiC

crystals formed at the surface of the SiC substrate for supplying the crystals layer at the top of the melt. This can explain the observations exposed herein with the dissolution of the substrate, the local formation and decomposition of larger SiC crystals close to the substrate and the development of a layer at the top of the melt. The driving force of the dissolution-growth of SiC crystals is a small thermal gradient inducing the dissolution of SiC on the hotter area to saturate the liquid, the diffusion of carbon along the thermal gradient and the growth of the SiC crystal in the colder area. No influence of the nature of the SiC substrate has been identified.

5. Conclusion

From these experimental results, the interaction between SiC and molten silicon appears to be strongly dependent on the temperature and on the thermal gradients. A coherent mechanism with two main stages is proposed according to the results of the experiments with dense SiC substrates. The molten C-saturated silicon induces a dissolution-growth of SiC crystals. The growth occurs mainly on the SiC coldest surfaces of the sample by dissolution of the hottest SiC areas. In order to homogenize the chemical composition, the carbon in solution diffuses along its chemical gradient, corresponding to the thermal gradient. The solubility of carbon in molten silicon decreasing with temperature, the liquid in colder areas is then supersaturated, what is responsible for the growth of large SiC crystals at the coldest areas. Two successive areas of growth have been identified: the surface of the starting SiC substrate and the SiC layer formed at the surface of the melt. The crystal growth of SiC in presence of molten silicon appears to be a substantial and complex phenomenon whose driving-force is the thermal gradient that could be very low. It would be better to take it into account in all processes bringing together these two phases because it could influence the overall evolution of the system and consequently the resulting properties. One of the actual challenges is to model such a chemical system by considering the thermal, thermodynamic and kinetic

phenomena that occur between a ceramic and a liquid. On this way this study gives some relevant results about the SiC-molten Si system.

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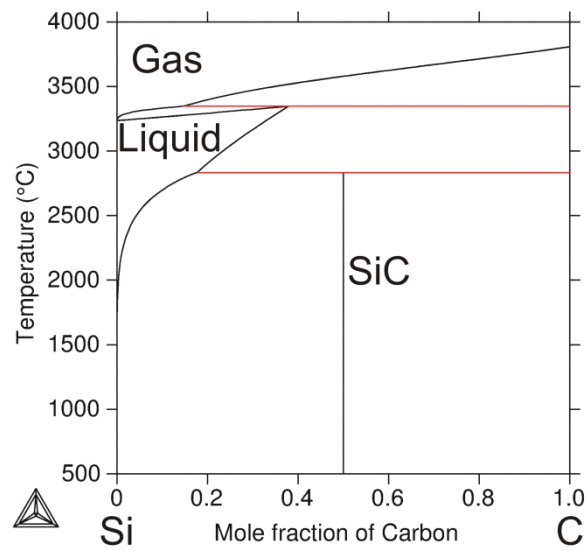


Figure 1. Calculated Si-C diagram [2,3].

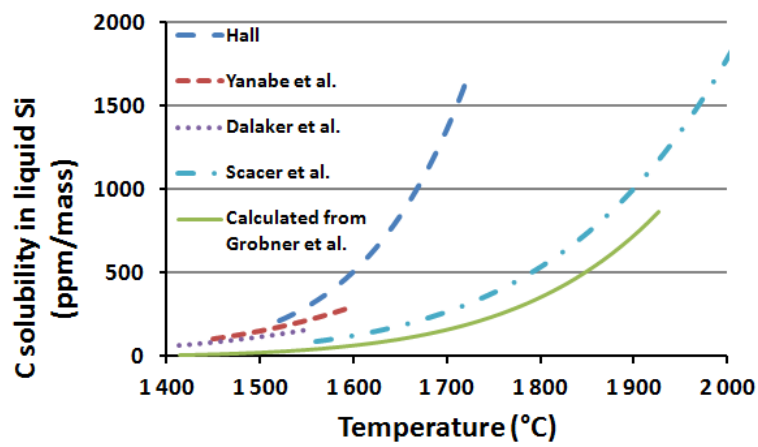


Figure 2. Solubility of carbon in molten silicon from literature [3, 30-33]. The values from Grobner et al. were calculated by using ThermoCalc software [2].

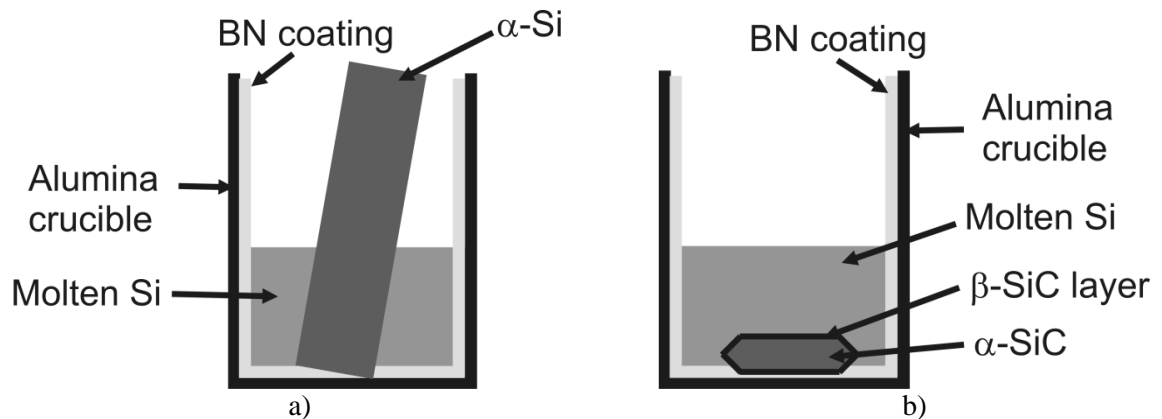
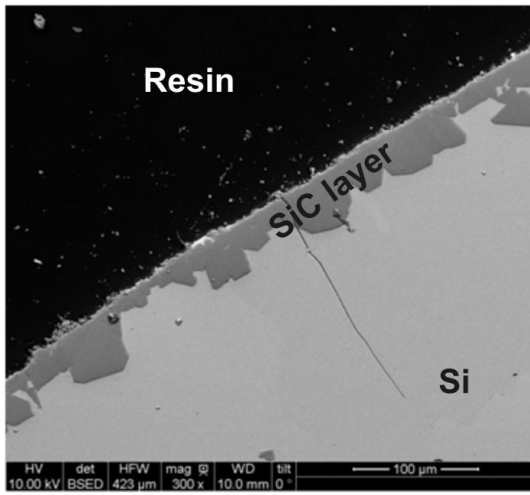
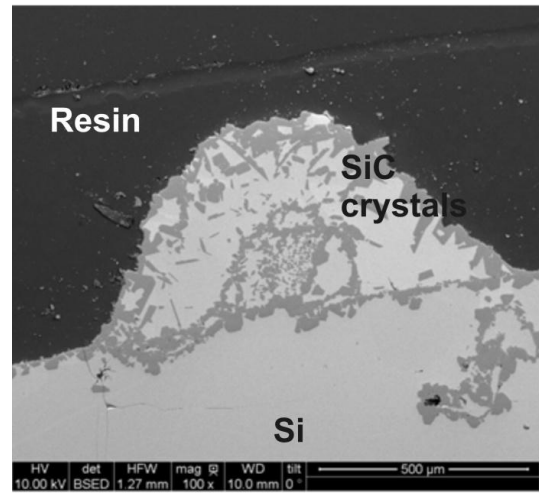


Figure 3. Schematic representations of the two different kinds of samples during a heat treatment at 1 or 1600°C in molten Si: a) α -SiC bar and b) α -SiC pellet with a coating of β -SiC



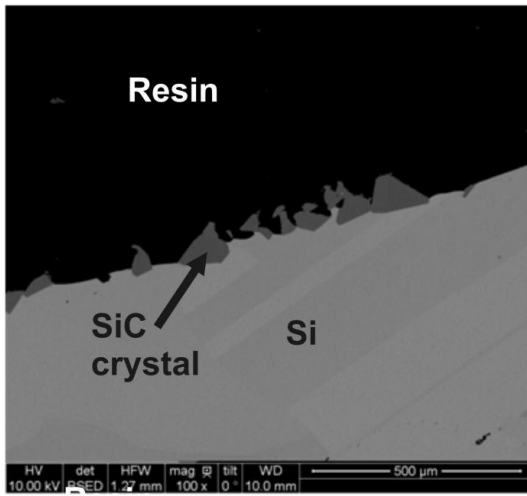
a)



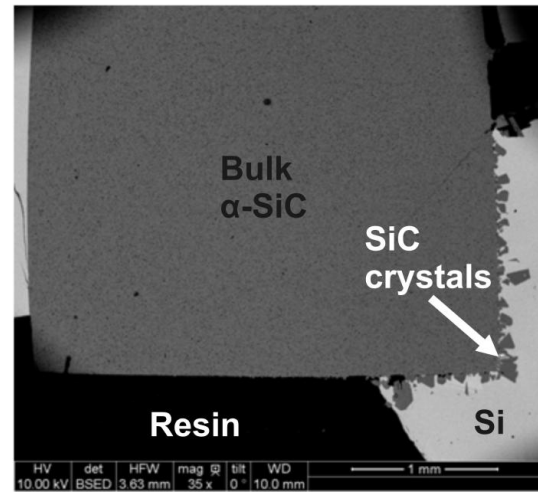
b)

Figure 4. Backscattered electrons images of pure silicon after 1600°C for 4h:

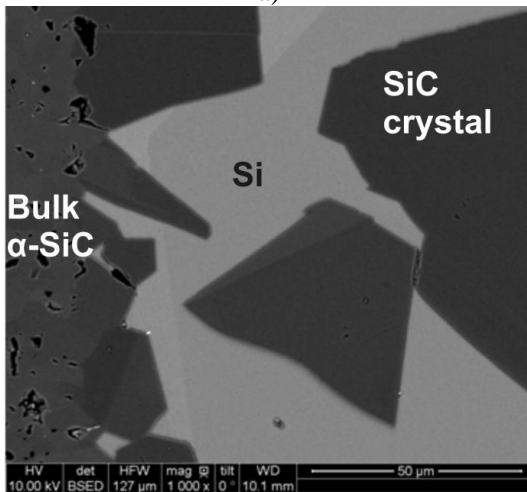
a) SiC layer at the surface, b) Si-SiC protuberance at the top.



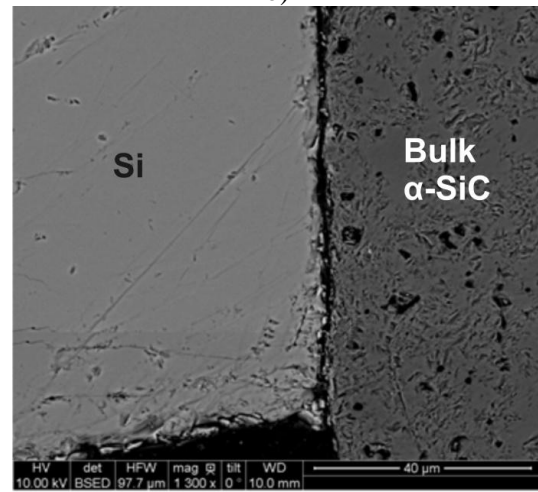
a)



b)



c)



d)

Figure 5. Backscattered electrons images of the SiC bar in silicon after 1450°C for 4h:

a) at the top of the Si melt, b) overall view of bottom of the sample,

c) at the interface SiC/Si on the left side, d) at the interface SiC/Si on the right side.

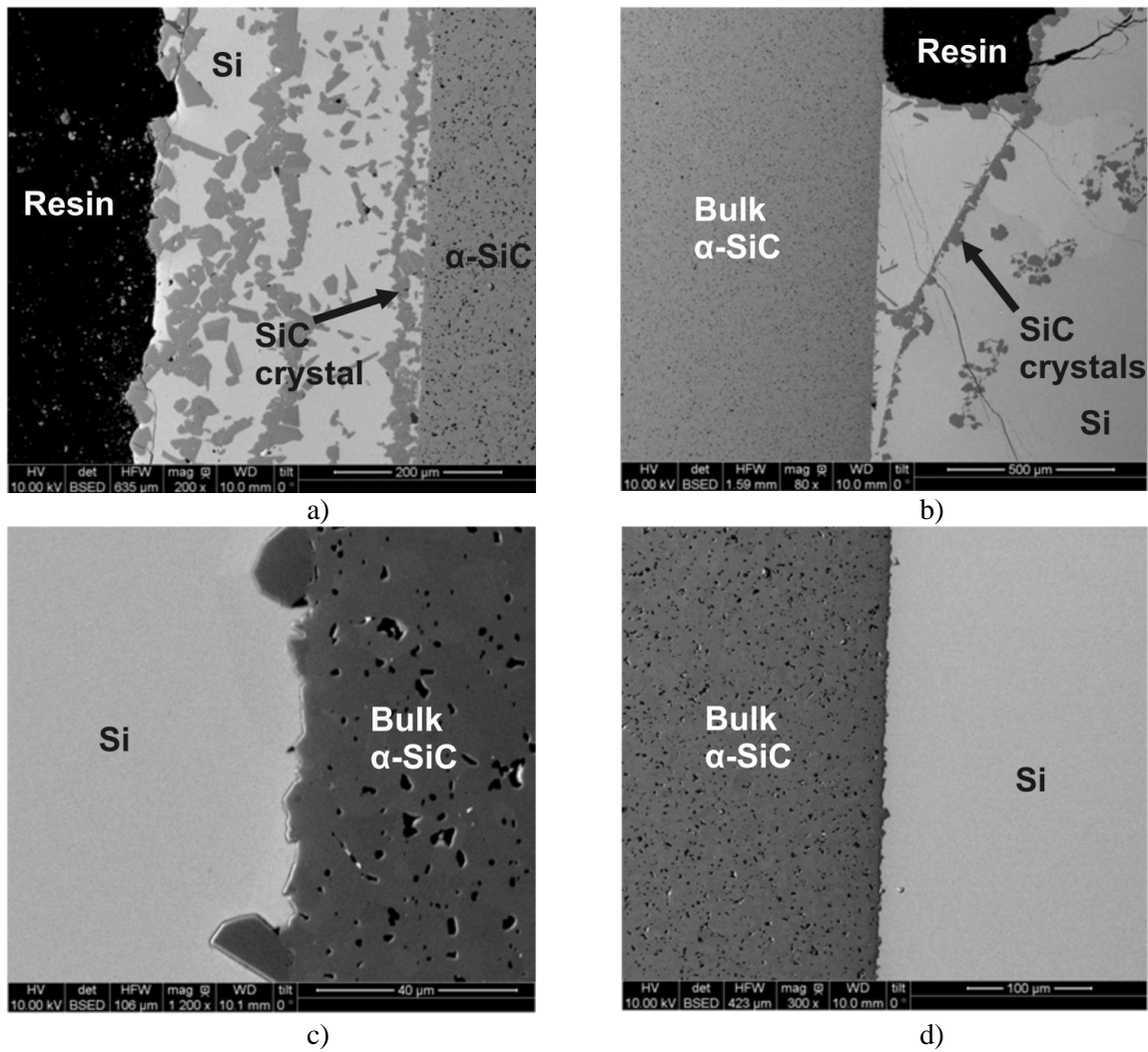


Figure 6. Backscattered electron images of the SiC bar in silicon after 1600°C for 4h:
a) at the surface of the non-immersed part, b) at the top of the immersed part,
c) at the left bottom of the immersed part, d) at the right bottom of the immersed part.

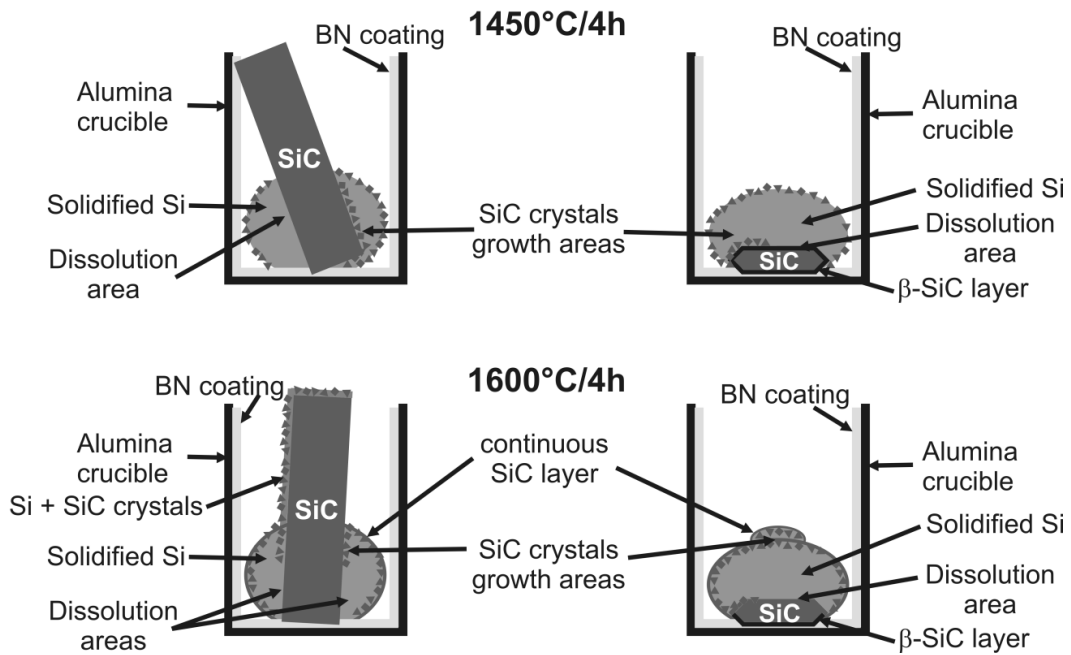
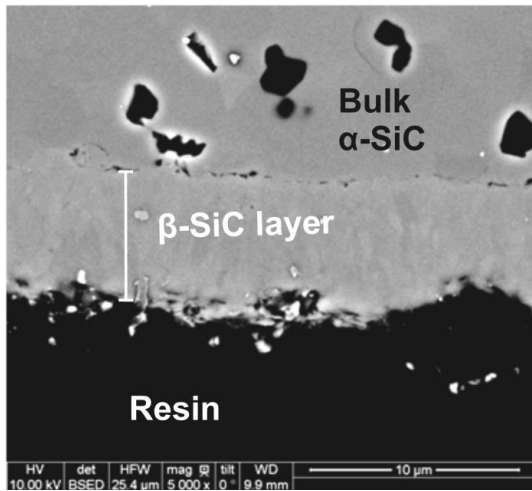
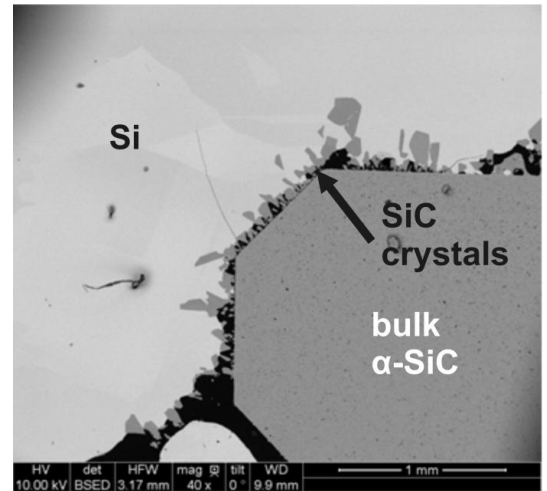


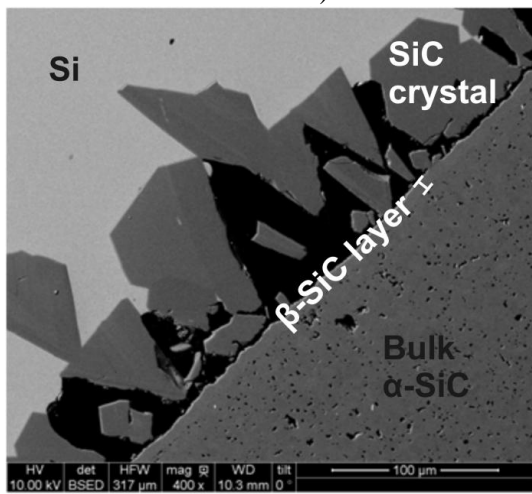
Figure 7. Schematic representations of the SiC dense samples after heating at 1450 or 1600°C for 4 hours. SiC bars samples are on the left side and the SiC pellets on the right side.



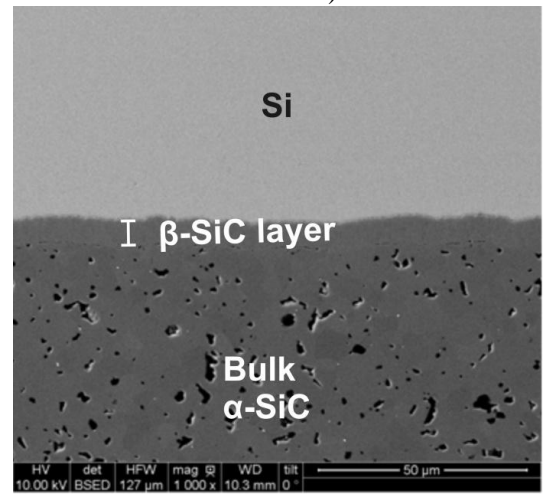
a)



b)

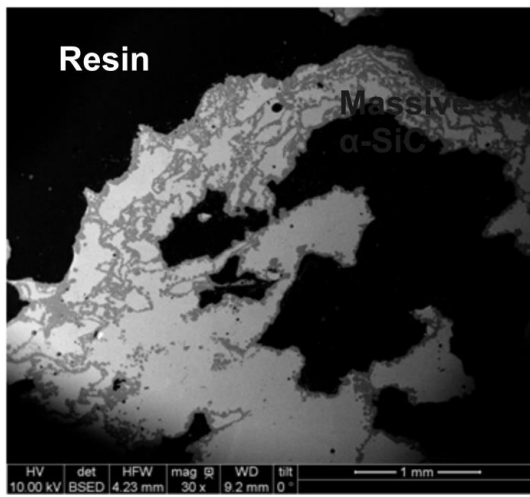


c)

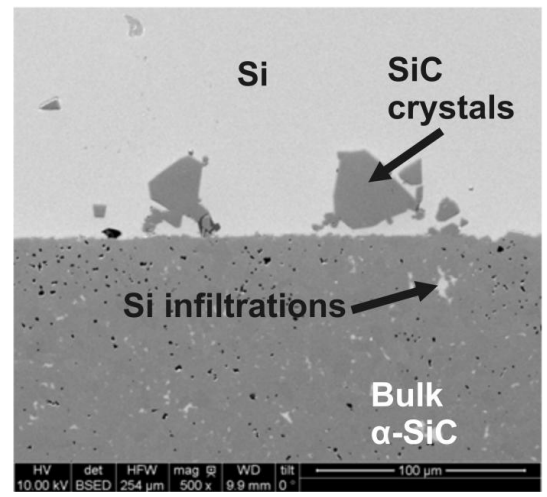


d)

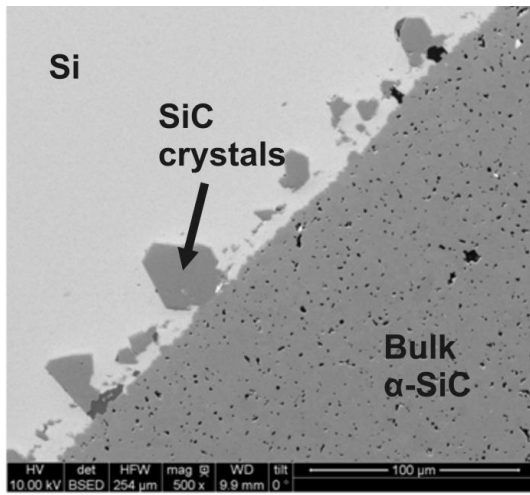
Figure 8. Backscattered electrons images of the SiC pellet in silicon after 1450°C for 4h:
a) at the bottom of the SiC pellet, b) overall view of the sample,
c) at the interface SiC/Si on the left side, d) at the interface SiC/Si on the upper right side.



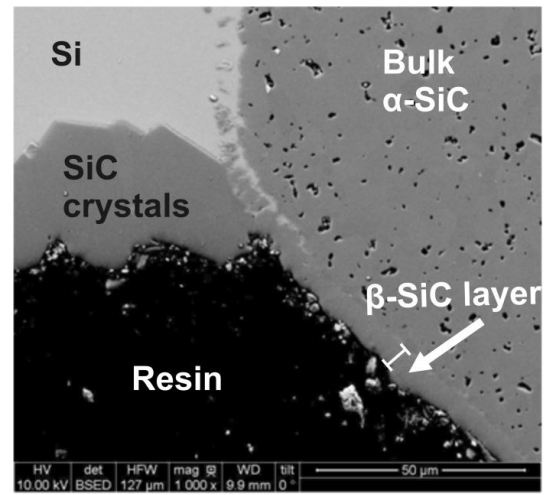
a)



b)



c)



d)

Figure 9. Backscattered electrons images of the SiC pellet in silicon after 1600°C for 4h:
a) at the top of the Si melt, b) at the interface SiC/Si on the upper part,
c) at the interface SiC/Si on the left side, d) at the interface SiC/Si on the bottom.

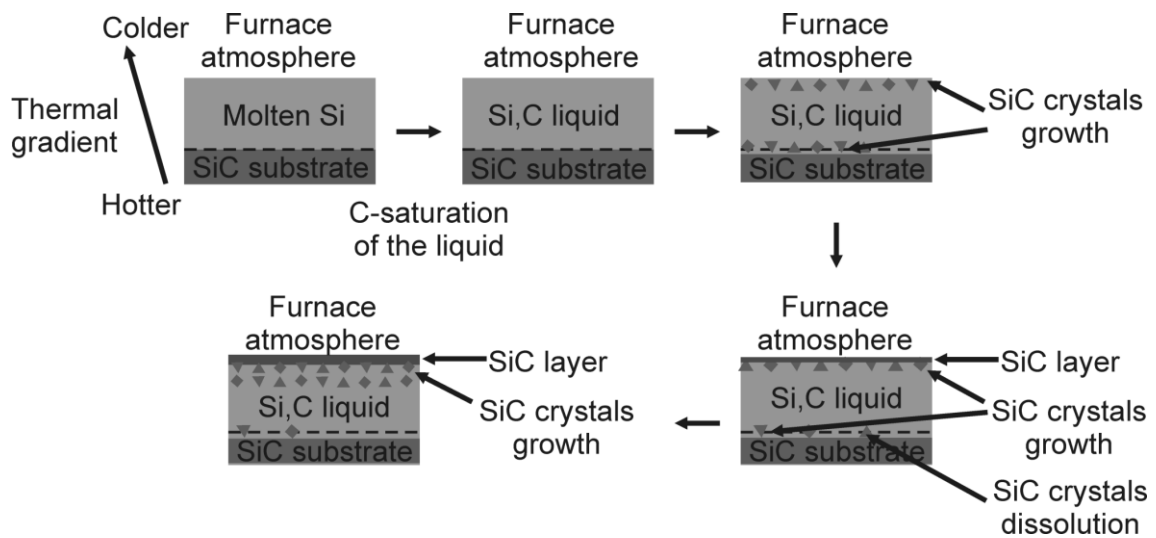


Figure 10. The stages of the interaction between dense SiC and molten Si.
In the present case, the atmosphere of the furnace is a source of carbon.