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An original way to investigate the siliconizing of carbon materials

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Abstract

The reaction of liquid silicon with glassy carbon and polycrystalline graphite was investigated according to two siliconizing processes. In the first process, the reactants are progressively heated from room temperature up to 1600 °C. In the second one, the liquid silicon is poured onto the carbon sample once the reactants have reached the required temperature, in order to consider short reaction times. Thus, an original equipment consisting of a graphite reactor, has been specially designed for this purpose. The nature and the growth rate of the resulting silicon carbide has been studied using scanning electron microscopy. The results showed the formation of a thin continuous layer of SiC crystallites at the liquid silicon/carbon interface. The thickness of the layer shortly becomes independent of reaction time (about 10 μm on glassy carbon and 15 μm on polycrystalline graphite after 30 min reaction time) while some isolated SiC particles appear in the solidified silicon phase, as well as a regular and unusual time dependent SiC layer at the silicon melt/atmosphere interface.

Keywords: D. Carbon; D. SiC; Graphite; Infiltration; Liquid silicon

1. Introduction

During space shuttle re-entry into an oxidative atmosphere, the nose cone can reach surface temperatures up to 1800 °C. Similarly, when an aircraft lands, the brakes can reach temperatures of up to 1000 °C. So, the materials involved demand a good wear resistance and high friction coefficients [1].

Silicon carbide, therefore, has become an up and coming high temperature material since there has been an increasing demand for high performance ceramics and composite materials.

Specifically, there has been a great deal of interest in reaction bonded silicon carbide coating on carbon materials [2–4]. This processing method has the advantages of combining thermal shock resistance, strength and fracture toughness of carbon/carbon materials, with low abrasive and oxidative wear, and a simple and short production route.

Reaction bonded silicon carbide coating on carbon materials can be obtained by melt infiltration of silicon into porous carbon/carbon preforms [3,5,6]. This process implies to control high temperatures because of the high melting point of silicon (1410 °C). Hence, there are only a few published data on the physical and chemical properties of liquid silicon [7–11], and the reaction of carbon with liquid silicon has essentially been studied in an empirical way, leaving some disagreement between the authors in the interpretation of the observed phenomena [2,12–16]. Mainly, two mechanisms are proposed.

Mechanism 1: the limiting step is the diffusion of carbon and silicon through SiC.

Fitzer [2] and Li [8] suggest a two stage mechanism. First, the heterogeneous nucleation and growth of SiC leads to the formation of a continuous polycrystalline SiC layer. Further growth of this layer is attributed to the diffusion of the reactive species through the silicon carbide coating. According to Li [8], the dissolution of carbon in liquid silicon takes place instantaneously, leading to the formation of Si–C clusters that can be preferentially adsorbed at

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the liquid/solid interface. After saturation of this adsorption layer by the Si–C clusters, a two-dimensional continuous SiC film forms through an heterogeneous nucleation and crystal growth process. The formation of this initial continuous SiC layer is very fast, and the subsequent growth is controlled by diffusion of C and/or Si through the SiC layer. Studies of diffusion of carbon and silicon in polycrystalline β-SiC have been carried out by Hon [17,18] and suggest that lattice self-diffusion coefficient for carbon is 50–100 times higher than for silicon. It is likely that the SiC layer growth proceeds by migration of carbon through SiC and consequent reaction at the SiC/Si interface. Several mathematical models are presented to describe the kinetics of the reaction [2,3,13]. Fitzer gives an equation for parabolic SiC layer growth depending on the diffusion coefficients of C and Si through SiC. Zhou found a four-power rate law and developed a model assuming the diffusion of carbon-ion vacancy through the SiC layer under an electric field as the rate-limiting step.

Mechanism 2: solution–precipitation process.

Pampuch and Ness suggest a solution–precipitation mechanism, in which carbon is dissolved into liquid silicon, and SiC subsequently precipitates from a supersaturated solution of carbon in silicon. According to Scace [10], the dissolution of carbon in liquid silicon is exothermic and the enthalpy of solution is −247 KJ/mol. Then the crystallization of β-SiC from supersaturated solutions of carbon in silicon should be an exothermic process, as the heat of reaction between carbon and liquid silicon is −115 KJ/mol [15]. The exothermic dissolution of carbon in liquid silicon causes a local temperature rise at the dissolution sites, which increases the solubility of the carbon causing further dissolution. The temperature gradient produced within the silicon causes a rapid diffusion of the carbon into the melt. The carbon diffuses to locally cooler sites where it precipitates as silicon carbide. According to Ness [14] the carbon may diffuse in the liquid silicon as C–Si pairs or even as CSi_4 units.

The purpose of this work is to describe the reaction mechanisms and parameters between different carbon materials and liquid silicon between 1450 and 1600 °C. Two different carbon materials have been selected for this study since they are generally used as references for their specific structural properties. First, glassy carbon has been chosen because it is isotropic, has a low density and only possesses a closed microporosity, so it is not infiltrated by liquids. Secondly, polycrystalline graphite has been selected because, unlike vitreous carbon, it undergoes liquid infiltration due to its micronic anisotropic structure and its important open porosity.

The first steps of the reaction kinetics of liquid silicon with glassy carbon and polycrystalline graphite were investigated according to two siliconizing processes :

1. In a conventional way, siliconizing was performed by placing into contact the carbon and the silicon at room temperature and heating the reactants up to 1600 °C. A siliconizing experiment carried on a glassy carbon sample held for 1 min at 1600 °C shows that a continuous silicon carbide layer has formed, and its thickness already attains several micrometers. This SiC layer has grown between the silicon melting point and 1600 °C, thus the actual reaction time was in fact about 1 h. Hence, the reaction of carbon with liquid silicon begins immediately after melting the silicon at 1410 °C, and infiltration of porous carbon preforms occurs within only a few seconds.
2. To avoid SiC formation during heating up to the determined temperature of treatment, another siliconizing process has been investigated and performed. For that purpose, an original graphite reactor was built, which allowed the silicon and the carbon samples to be heated to 1600 °C without coming into contact. Once the temperature became constant, the liquid silicon was poured onto the substrate. This system allowed us to investigate the siliconizing at a given temperature during very short times.

2. Experimental

The glassy carbon (CV 25) plates, treated at 2500 °C, with a density of 1.4 and a thickness of 2.5 mm were supplied by Carbone Lorraine. Square pieces (10×10×2.5 mm) were cut into these plates.

The polycrystalline graphite ATJ supplied by Union Carbide was used in the form of cylindrical crucibles. The outer diameter of the crucibles is 19 mm, the height is 21 mm, and the walls thickness is 2 mm. The graphite contains less than 5 ppm of impurities. Graphite samples with two different pore sizes were siliconized.

Silicon powders (purity 98%) with two different particle size ranges ($Ø > 100$ μm and $50 < Ø < 250$ μm) were supplied by Eckart-Poudmet.

Two groups of siliconizing experiments were carried on.

The first group refers to the experiments conducted in a standard alumina tube, part of a furnace provided with $LaCrO_3$ resistors. The silicon powder was put on the vitreous carbon plate or in the graphite crucible, introduced in an alumina cup, at room temperature, and loaded into the alumina tube, which was evacuated under a vacuum of 10^{-2} mbar. The sample was then heated to 1500 or 1600 °C at a heating rate of 5 °C/min

and held for a given time period (5 min to 3 h) under an argon flow of a total pressure of 1 atm. This process is called "progressive siliconizing" (A).

The second group refers to the experiments conducted in the original graphite reactor presented in Fig. 1 and is named "direct siliconizing" (B). A funnel is placed over a crucible containing the carbon substrate. The silicon powder is set in an alumina crucible, which is kept in a vertical position. All the graphite parts constituting the reactor, except the alumina crucibles containing the silicon and the vitreous carbon, were realised in our laboratory. The total height of the graphite reactor is 150 mm. It needs to be placed precisely in the alumina tube of the furnace. The reactor is heated to 1000 °C at a constant heating rate of 7 °C/min under a vacuum of 10^{-2} mbar to remove air and degas the sample, and from 1000 °C to 1600 °C at a rate of 5 °C/min under an atmosphere of argon. The furnace temperature is kept constant at 1600 °C for 30 min to obtain a homogeneous silicon melt. The crucible containing the liquid silicon is then rotated, allowing the liquid silicon to flow out onto the carbon substrate. The temperature is kept constant for different reaction times (1 to 150 min) and then quenched to 1200 °C, followed by a linear cooling rate of 5 °C/min down to room temperature. The temperature was measured with a Pt/Pt + 10% Rh thermocouple located under the graphite reactor.

After reaction, the samples were cut into two pieces and one-half was polished with SiC abrasive discs to be observed by scanning electron microscopy (SEM; Phillips XL 30). The reaction product is characterized by SEM and the average thickness of the SiC layer was directly measured using the SEM micrographs. Between three and five micrographs were taken of each cross-section and an average of 25 values for the SiC layer thickness per micrograph.

In order to remove residual silicon and to reveal the reaction product, some of these samples were etched with a mixture of nitric acid (100%) and hydrofluoric acid (40%).

The phase analysis of the reaction products was carried out by X-ray diffraction (Inel XRG 3000) using CuK_α radiation.

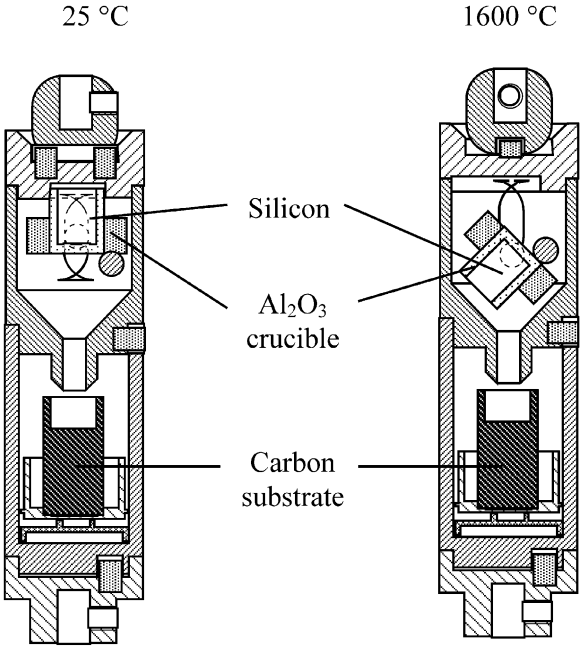

Fig. 1. Original graphite reactor for "direct siliconizing" (B).

3. Results and discussion

3.1. Reaction between liquid silicon and glassy carbon

The SEM micrographs (Fig. 2) show no penetration of liquid silicon into glassy carbon, but the formation of a continuous SiC layer at the silicon/carbon interface after 90 min at 1600 °C (A). This layer forms a barrier separating the carbon from the residual silicon.

From the numerous experiments involving the glassy carbon/liquid silicon system, four main phenomena have been observed:

1. the fast formation of a continuous SiC layer with variable thickness,
2. the layer growth seems to break after about 30 min reaction time. After 24 h of reaction at 1600 °C (Fig. 3), the SiC layer thickness is the same as after 30 min of reaction.
3. the appearance of SiC outgrowths near the solid/liquid interface, and in some cases, isolated SiC particles dispersed in the silicon phase (Fig. 4).
4. the formation of a thick SiC layer at the liquid silicon/argon interface, growing steadily with reaction time (Fig. 3).

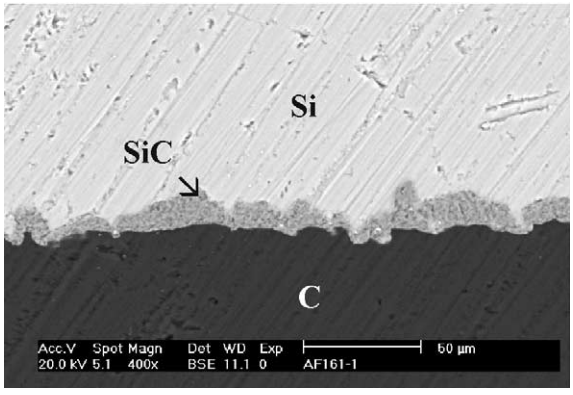

Fig. 2. Glassy carbon siliconized up to 1600 °C with a hold of 90 min (A), ×400.

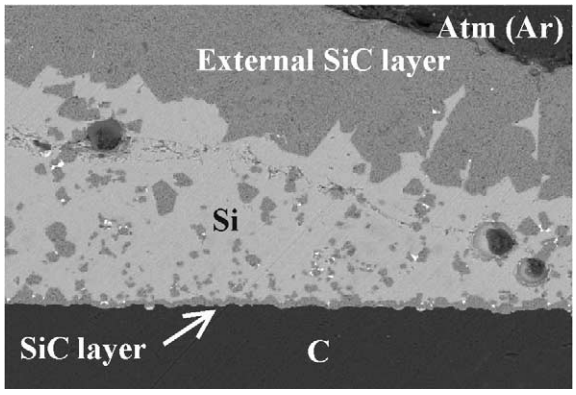

Fig. 3. SiC reaction-product at the C/Si and Si/Ar interfaces after a hold of 24 h at 1600 °C (A), ×100.

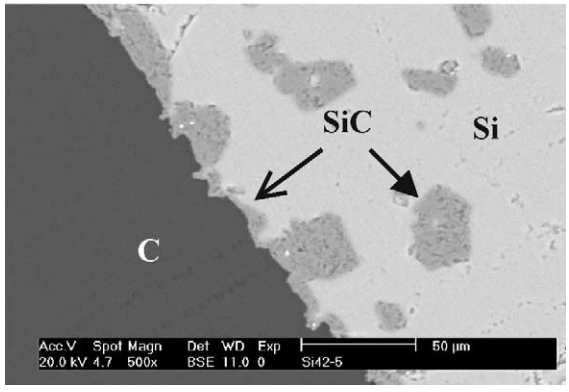

Fig. 4. SiC outgrowths and isolated particles in the Si phase after 7 min of siliconizing at 1600 °C (B), ×500.

3.2. Progressive siliconizing

The reaction rate of the silicon/glassy carbon "progressive" reaction is plotted in Fig. 5 as the average thickness of the continuous SiC layer versus time at 1500 °C [Fig. 5(a)] and 1600 °C [Fig. 5(b)]. It shows that most of the SiC was formed during very short reaction times, up to 30 min. The thickness of the SiC layer remains nearly constant, about 10 μm, with longer reaction times. These results are almost similar at 1500 and 1600 °C, and are in agreement with those of other authors [13,19] as Deike who reports a SiC thickness layer of about 8 μm on glassy carbon after 48 h at 1500 °C. Two samples were held at 1600 °C up to 12 and 24 h, the average SiC thickness is 12 and 7 μm, respectively, and moreover it can be seen a great amount of isolated SiC particles scattered in the solidified silicon phase (Fig. 3). This means that the SiC thickness does not increase anymore with reaction time, and can even decrease due to its fragmentation. An explanation of the mechanism will be given later.

The SEM pictures (Figs. 6 and 7) represent, respectively, the glassy carbon siliconized surface and the glassy carbon polished cross-section after an HF/HNO_3 etching to remove residual silicon [20,21]. In the case of the cross-section sample, the silicon is only partly removed in the depth, on the sample surface. Fig. 6 reveals a uniform coating consisting of adjacent but randomly oriented crystallites identified by X-ray diffraction as the cubic β-silicon carbide phase. The analysis by X-ray diffraction only reveals the presence of the cubic SiC phase. The continuous SiC layer seems to be a rough monolayer of SiC crystals casually arranged onto the carbon surface. After 12 and 24 h reaction time, some faceted, hexagonal, shaped SiC crystals appear at the liquid/solid interface, adjacent to the SiC layer (Fig. 7).

On the other side, a silicon carbide layer appears at the liquid silicon/argon interface and its thickness can reach 150 μm after 24 hours of reaction time (Fig. 3). Both SiC layers formed at the carbon/silicon and the silicon/argon interfaces exhibit the same crystalline structure. The SiC layer formed at the silicon/argon interface, whose thickness increases with reaction time, is composed of larger crystallites than previously, up to

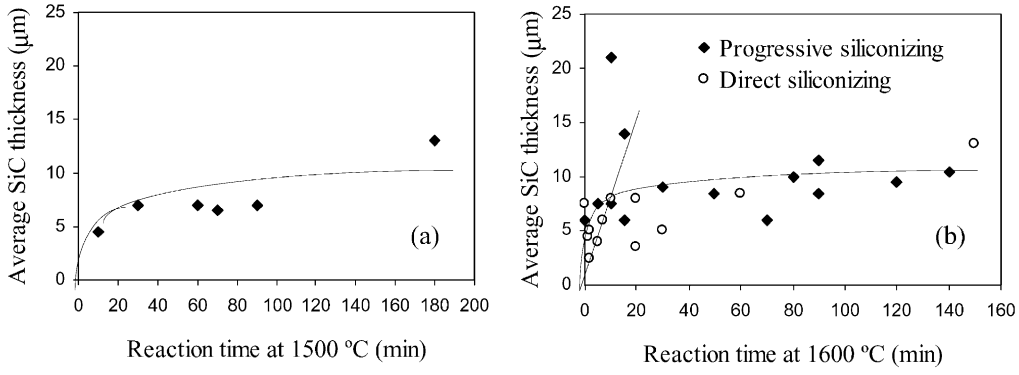

Fig. 5. Thickness of the SiC layer as a function of the reaction time (a) at 1500 °C for "progressive" and (b) at 1600 °C for "progressive" and "direct" siliconizing of glassy carbon.

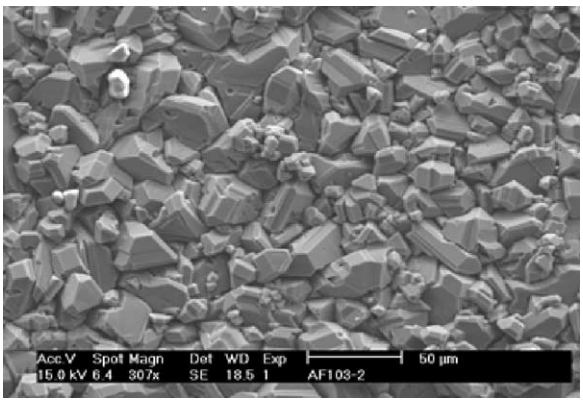

Fig. 6. Glassy carbon surface after a hold of 1 h siliconizing at 1600 °C (A) and subsequent acid etching, ×300.

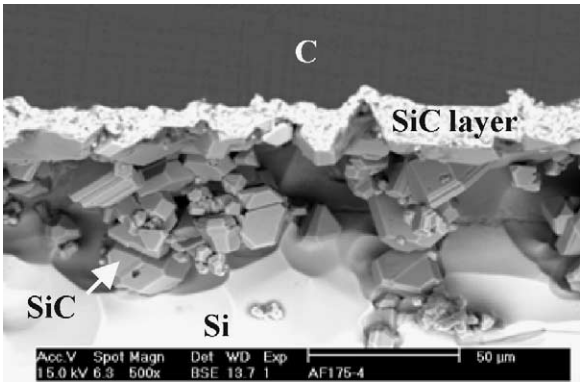

Fig. 7. Glassy carbon cross-section after siliconizing with a hold of 12 h at 1600 °C (A) and subsequent acid etching, ×500.

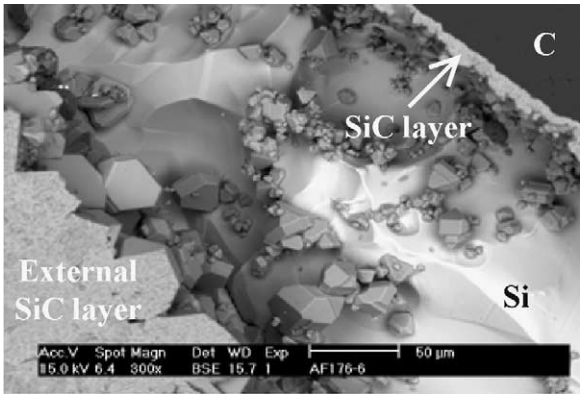

Fig. 8. SiC reaction-product at the C/Si and Si/Ar interfaces after siliconizing with a hold of 24 h at 1600 °C (A) and subsequent acid etching, ×300.

50 μm in diameter after a hold of 24 h at 1600 °C (Fig. 8).

3.3. Direct siliconizing

The thickness of the SiC layer resulting from direct siliconizing is represented in Fig. 5(b) as a function of the reaction time for the silicon/glassy carbon system at 1600 °C. The growth rate of the SiC layer is very high at the very first stage of the reaction. A thickness of 4 μm is reached within *less than 5 min* of contact between the reactants, and the average layer thickness is about 10 μm after 1 h. In that case, the actual time of reaction between liquid silicon and carbon can be less than five min, whereas for the corresponding time of reaction (5 min) in the case of progressive siliconizing the effective reaction time is 1 h between 1410 and 1600 °C.

So, it can be concluded that the silicon carbide formation *proceeds mainly within the first min of contact*, the primary SiC layer separates the liquid silicon from the carbon and therefore, prevents further reaction. The subsequent growth of the silicon carbide layer then should be controlled by the diffusion of either carbon or silicon through the SiC layer. Many authors describe the siliconizing process as a heterogeneous solid/liquid reaction followed by a mechanism of diffusion of the reactants [2,12,13] through the SiC layer. Different kinetic models were developed to explain the observed SiC growing rate [2,3,13]. The first step is a period of rapid growth corresponding to a mechanism of heterogeneous nucleation and subsequent growth on the carbon surface. This is reflected by the initial linear region of the curve displaying the time dependence of the SiC formation. Once the continuous polycrystalline SiC layer has been built, the following growth is ensured by the diffusion of carbon and/or silicon species through SiC, thereby considerably reducing the reaction rate, due to the small diffusion coefficient values of C and Si through SiC [17,18]. This standard model is usually adopted to explain the collapsing reaction rate after passivation of the reactive surface. But, this explanation does not take into account the presence of the isolated SiC particles in the silicon phase in our case. If such a rate-limiting step is considered for the SiC growth, the appearance of the SiC grains must be dealt with another mechanism and/or may involve another carbon source. The polishing procedure must be considered as a way to introduce some particles on the sample surface. However, the SiC particles are strongly integrated into the silicon phase. Besides, the acid etching shows evidence of the presence of isolated SiC particles deeply incorporated in the solidified silicon. To explain the presence of these SiC particles, we can consider a high reaction rate even after the formation of the primary SiC layer. After the nucleation and growth of SiC crystallites on the carbon surface, the substrate is protected against the liquid silicon corrosion. At the grain boundaries the growth of the SiC crystallites generates high compression forces, leading to the break of the SiC layer into SiC particles scattered in the liquid silicon. The SiC formation goes through a succession of growing SiC periods followed by local breaks of the SiC layer.

3.4. Reaction between liquid silicon and polycrystalline graphite

The SEM pictures (Fig. 9) show that liquid silicon sweeps into the pores of the graphite and that the transformation of silicon into silicon carbide occurs on the pores walls. The siliconizing process involves two steps, the infiltration of the liquid silicon into the preform, and the reaction of liquid silicon with graphite to form silicon carbide. These phenomena occur immediately after the melting of silicon.

The porous graphite is characterised by an important open macroporosity, with pore size up to 300 μm. As a consequence, the whole amount of liquid silicon penetrates into the porous channels, and fills the pores (Fig. 10, the bottom and right part correspond to the cross-section of the crucible and top left hand to the inside bottom of the crucible). Similarly, due to the smaller average pore size of some less porous graphite samples, the flow of liquid silicon through the narrow capillary channels leads to the formation of silicon carbide on the capillary walls, causing choking off and stopping the flow. The resulting infiltration depth is widely lower than in the usual porous graphite crucibles, as shown in Fig. 11. The cavity inside is still filled with solidified silicon, and a continuous silicon carbide coating has appeared at the C/Si interface, filling the channels.

The SiC layer thickness variation as a function of the reaction time is presented in Fig. 12 for the less porous graphite samples progressively and directly siliconized at 1600 °C. The general evolution trend of the curves is similar to those of the silicon/glassy carbon system. The average SiC layer thickness is slightly higher (~12 μm), and the coating is much more irregular than previously. The diagram representing the extent of reaction versus time for the direct siliconizing process of graphite confirms a high reaction rate during the first min of the reaction.

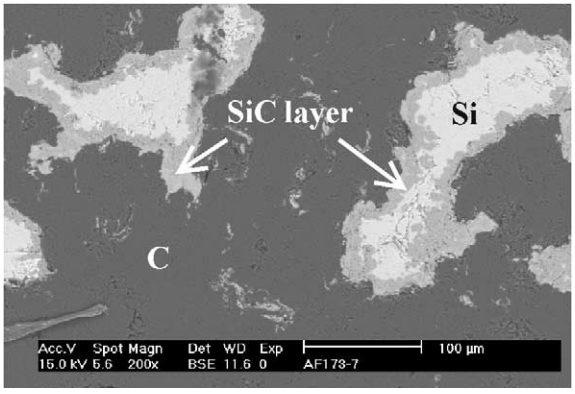

Fig. 9. Si infiltration and SiC reaction product at the pore walls of porous graphite after siliconizing at 1600 °C with a hold of 1 h (A), ×200.

The SiC layer formed at the C/Si interface appears highly irregular due to the high porosity and anisotropy of the graphite material compared to the smooth glassy carbon surface (Fig. 13). As the infiltration of liquid silicon and the siliconizing reaction occurs simultaneously, the resulting silicon carbide layer is formed of *oriented crystals in relation with the graphite particles*, and consequently, with little cohesion and adherence on the substrate. The chemical transformation of carbon into silicon carbide induces an important volume increase of the solids and the formation of cracks and flaws in the SiC coating [22]. These new channels provide a supplementary pathway for the liquid silicon flow, while shrinkage of the capillary channels may also provoke local choke off. These corrosion waves can lead to a cleavage of the graphite substrate, which is emphasised by the foliated structure of the graphite (Fig. 14). This is confirmed by the presence in the solidified silicon phase, of an alignment of large isolated SiC crystals in the vicinity of the SiC layer (Fig. 13), probably related to the local breakdown of the SiC layer.

Several hypotheses may contribute to clarify the presence of the independent SiC crystallites in the silicon phase. One of them is the possible dissolution and pre-

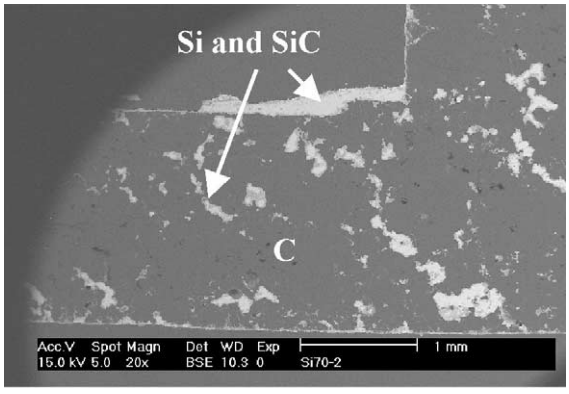

Fig. 10. Porous graphite crucible cross-section after 7 min siliconizing at 1600 °C (B), ×20.

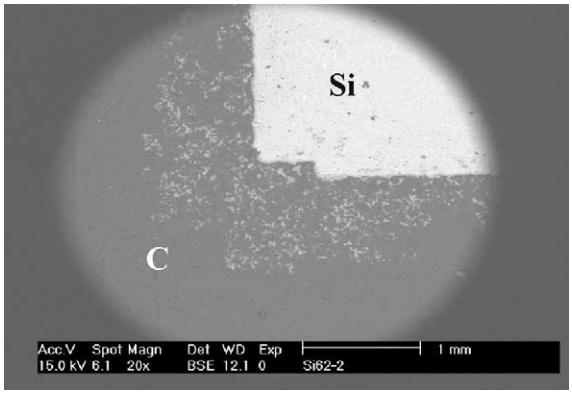

Fig. 11. Non porous graphite crucible cross-section after 15 min siliconizing at 1600 °C (B), ×20.

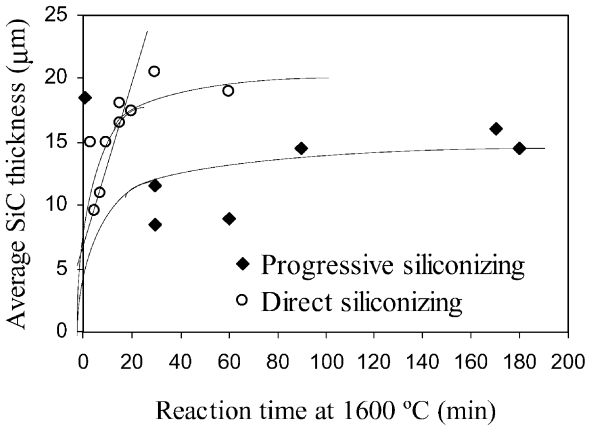

Fig. 12. Thickness of the SiC layer as a function of the reaction time for "progressive" and "direct" siliconizing of graphite at 1600 °C.

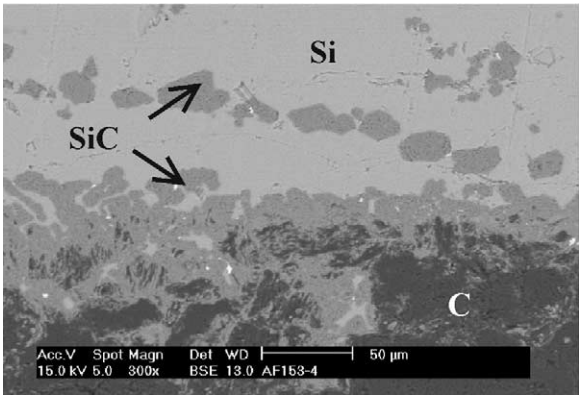

Fig. 13. Morphology of the reaction-formed SiC after siliconizing of graphite with a hold of 90 min at 1600 °C (A), ×300.

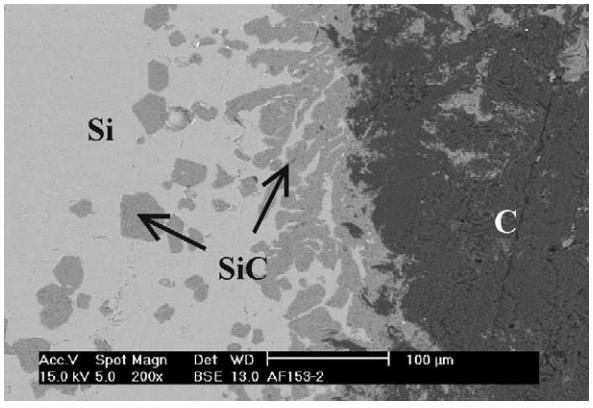

Fig. 14. Morphology of the reaction-formed SiC after siliconizing of graphite with a hold of 90 min at 1600 °C (A), ×200.

cipitation of the SiC layer formed at the Si/SiC interface. Although the Si/SiC system is supposed to be chemically inert, the wetting angle of liquid silicon on silicon carbide is rather low, about 30–45° at 1430–1450 °C [23] and some authors report the dissolution of SiC in liquid silicon [2,22,23]. The extended contact of the reactive liquid makes the SiC layer brittle, allowing the silicon to infiltrate between the SiC crystals. But, this assumption does not explain why almost no isolated SiC particles can be observed in the graphite pores filled with solidified silicon as seen in Fig. 9 which presents the cross-section of a siliconized porous graphite crucible. The coating formed on the walls of the pores is similar in appearance to the SiC layer at the carbon/silicon interface in the crucible, but no separated SiC particles can be observed. Thus, the chemical corrosion of the SiC coating does not alone explain the appearance of the isolated SiC crystallites. One can consider the building of a SiC layer with a large volume increase on a "flat" surface or on a closed cylindrical surface. In the first case, internal stresses due to the chemical reaction induce cracks and fragmentation of the layer, while in the second case, these concentric stresses are absorbed in the bulk of the material and locally provoke high pressures which limit further reaction.

3.5. External SiC layer

Concerning the SiC layer at the liquid silicon/atmosphere interface, a few authors relate the formation of such a layer based on the precipitation of SiC from a carbon supersaturated liquid silicon solution [24], or when using an argon/CO gas mixture to constitute an equilibrium between Si and SiC [25]. During the synthesis of polycrystalline silicon thin films on graphite substrates by a zone melting recrystallization process at 1410 °C, Hauttmann [24] observes either a discontinuous or a continuous β-SiC crystals layer at the silicon/atmosphere (pressure of 10^{-5}–10^{-6} mbar) interface. The SiC particles size varies from 15 to 300 nm. The authors attribute the formation of this SiC layer at the interface to a heterogeneous nucleation process when the concentration of carbon in the silicon melt reached saturation, the carbon dissolved in the melt originating from the graphite substrate. Other authors [25] use an argon/CO gas mixture to form a SiC film at the silicon melt surface, the crucible containing the silicon being in silicon carbide. In that case, the carbon originates from the gaseous medium:

$$2\,Si_{(L)} + CO_{(G)} \rightleftarrows SiC_{(S)} + SiO_{(G)} \quad (1)$$

In our case, the carbon forming the silicon carbide at the silicon/argon interface originates from the carbon substrate or from the graphite reactor through a gaseous chemical reaction. In order to determine the carbon source, a few complementary experiments have been performed at 1600 °C:

1. The alumina crucible containing the silicon is placed in a graphite crucible, without any carbon sample.

2. The alumina crucible containing the silicon is placed in the graphite reactor described in Fig. 1, without any carbon sample.
3. The silicon powder is placed in an alumina crucible, without any carbon in the furnace.
4. The silicon powder is placed in a graphite crucible.

The cross-section of the samples is observed by SEM.

A silicon carbide layer is observed at the silicon/argon interface for samples 1 and 2. The thickness is 40 and 50 μm after a hold of 60 and 30 min at 1600 °C respectively, which suggests that it depends on the accessible graphite surface. No SiC layer has been observed at the silicon/argon interface for samples 3 and 4. In the case of the experiments 1, 2 and 3, there is no contact between the liquid silicon and the solid carbon, but for samples 1 and 2 graphite surfaces are present in the vicinity of the liquid silicon. Yet the alumina crucible is directly in contact with carbon, the reduction of alumina by carbon can be excluded from the reaction scheme.

Thus, these results indicate that the surrounding graphite contributes to the formation of the silicon carbide layer at the silicon/argon interface. This implies the formation of gaseous species such as CO and CO_2 to transport the carbon. Three sources of oxygen can be considered as the incomplete initial purging of the furnace tube can be excluded:

1. the small porosity of the alumina tube can cause oxygen from the atmosphere to enter in the reactor.
2. the oxygen present as an impurity in argon.
3. a chemical reaction involving the alumina from the reactor tube and the crucible containing the silicon.

For both progressive and direct siliconizing, the furnace tube is evacuated under a vacuum of 10^{-2} mbar prior to the argon flow. The oxygen content is less than 5 ppm, but can initiate a chain reaction involving the carbon oxides. Paccaud [26] has observed the oxidation of a silicon carbide coating due to the oxygen impurity content of argon.

Alumina (melting point = 2040 °C) is relatively inert, but can react with silicon at 1800 °C under vacuum [27]:

$$Al_2O_{3(S)} + 2\ Si_{(L)} \rightarrow Al_2O_{(G)} + 2SiO_{(G)} \quad (2)$$

through a three-stages reaction:

1. dissolution of alumina in liquid silicon;
2. diffusion of Al and O towards the silicon/argon interface; and
3. formation and evaporation of the gaseous Al_2O and SiO species.

Turovskii [11] mentions that 0.3–0.4 wt.% of aluminium was dissolved when liquid silicon was maintained in an alumina crucible at 1440 °C for 2 h.

According to the chemical species present in the reactor at 1600 °C, the following equilibriums should be considered:

$$2\ Si_{(L)} + CO_{(G)} \rightleftarrows SiC_{(S)} + SiO_{(G)} \quad (3)$$

$$Si_{(L)} + 2CO_{(G)} \rightleftarrows SiC_{(S)} + 2CO_{(G)} \quad (4)$$

$$2Si_{(L)} + CO_{(G)} \rightleftarrows C_{(S)} + SiO_{(G)} \quad (5)$$

$$2Si_{(L)} + CO_{2(G)} \rightleftarrows C_{(S)} + 2SiO_{(G)} \quad (6)$$

$$SiC_{(S)} + CO_{2(G)} \rightleftarrows 2C_{(S)} + SiO_{(G)} \quad (7)$$

$$SiC_{(S)} + CO_{2(G)} \rightleftarrows C_{(S)} + SiO_{(G)} + CO_{(G)} \quad (8)$$

At 1600 °C, the formation of $CO_{2(G)}$ is insignificant compared to the formation of $CO_{(G)}$. Therefore, the equilibriums (4), (6) and (8) are not taken into account.

The gaseous specie $Si_{(G)}$ should also be considered as the silicon vapour pressure at 1600 °C is not negligible [28]. A silicon carbide film is formed on the walls of the graphite reactor, which indicates the presence of silicon gaseous compounds ($Si_{(G)}$, $SiO_{(G)}$).

If the SiC layer at the silicon/argon interface is formed via the carbon of gaseous CO, then a diffusion process of the species $CO_{(G)}$, $Si_{(L)}$, $Si_{(G)}$ or $SiO_{(G)}$ must take place. Such a diffusion process of CO and SiO through a SiC layer has already been reported when forming a silicon carbide coating on a carbon substrate through reactive pack cementation [26]. A mixing of SiC and SiO_2 powders was heated to 1600 °C under an argon flow at a pressure of 1 bar. The reaction leads to the formation of a homogeneous SiC coating of a thickness of 80 μm after 90 min. The authors [26] favour a reaction mechanism involving solid/gas interactions between silicon carbide and SiO and O_2, formed when silica vapourizes. $SiO_{(G)}$ diffuses through the SiC layer, allowing the reaction of formation of SiC to take place at the C/SiC interface (equilibrium 7). The formed CO then diffuses through SiC towards the SiC/argon interface.

In our experiments, the CO formed via the carbon of the graphite reactor, can immediately react with the liquid silicon [equilibria (3) and (5)] and lead to SiC. The growth rate of the SiC layer is then controlled by the diffusion of $CO_{(G)}$, $Si_{(L)}$, $Si_{(G)}$ and $SiO_{(G)}$ through SiC. The diffusion coefficient of liquid silicon in SiC is very small and 100 times lower than that of carbon [17]. According to the morphology of the outgrown SiC crystals, the SiC growth seems to originate at the SiC/Si interface through the diffusion of $CO_{(G)}$ through the SiC layer, with the formation of $SiO_{(G)}$ which can diffuse back or react carbon scarcely dissolved in liquid

silicon. Thus, the growth of the SiC layer mainly depends on the carbon monoxide diffusion process.

But, as the silicon melt is saturated with carbon, it is not easy to estimate the contribution of these two reaction paths in the formation of the isolated SiC grains.

4. Conclusion

The reaction of liquid silicon with glassy carbon and polycrystalline graphite apparently leads to the formation of a continuous *time independent* β-SiC layer at the carbon/silicon interface. An original graphite reactor was developed to determine the reaction kinetics at the very first stages of the reaction. The morphology of the SiC layer is similar for both glassy carbon and graphite, but the latter undergoes infiltration of the liquid silicon in the porosity and local cleavage of graphite particles, which increases the fragmentation of the SiC coating. The development of the SiC layer on glassy carbon seems to be controlled by a mechanism similar to that for the graphite. The time independent thickness of the layer as well as the presence of isolated SiC crystals in the silicon phase, is in contradiction with the assumption of a growth mechanism only controlled by the diffusion of the reactants through the SiC layer. Hence, a mechanism of alternating periods of crystallization and fracture of the SiC layer would be more able to describe the observed phenomena. These results can be related to the results obtained by Birkel [29] who studied the corrosion of carbon materials by liquid aluminium at 800 °C. He observed a progressive peeling of the aluminium carbide Al_4C_3 layer starting below 500 h of reaction. The maximum thickness of the carbide layer is about 200 μm after more than 5000 h.

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References

[1] W. Krenkel, CMC Materials for High Performance Brakes, Extended Abstracts, ISATA Conference on Supercars, Aachen, Germany, 1994.
[2] E. Fitzer, R. Gadow, Fiber-reinforced silicon carbide, Am. Ceram. Soc. Bull. 65 (2) (1986) 326–335.
[3] F.H. Gern, R. Kochendörfer, Liquid silicon infiltration: description of infiltration dynamics and silicon carbide formation, Composites Part A 28A (1997) 355–364.
[4] W. Krenkel, F. Gern, Microstructure and characteristics of CMC Manufactured via the Liquid Phase Route, Extended Abstracts, ICCM9, Madrid, Spain, 1993, pp. 173–181.
[5] Y.M. Chiang, R.P. Messner, C.D. Terwilliger, D.R. Behrendt, Reaction-formed silicon carbide, Mater. Sci. Eng. A144 (1991) 63–74.
[6] O. Yamamoto, T. Sasamoto, M. Inagaki, Antioxidation of carbon-carbon composites by SiC concentration gradient and zircon overcoating, Carbon 33 (4) (1995) 359–365.
[7] J.G. Li, H. Hausner, Wetting and infiltration of graphite materials by molten silicon, Scripta Metall. Mater. 32 (3) (1995) 377–382.
[8] J.G. Li, H. Hausner, Reactive wetting in the liquid-silicon/solid-carbon system, J. Am. Ceram. Soc. 79 (4) (1996) 873–880.
[9] T.J. Whalen, A.T. Anderson, Wetting of SiC, Si_3N_4 and carbon by Si and binary Si alloys, J. Am. Ceram. Soc. 58 (1975) 396–399.
[10] R.I. Scace, G.A. Slack, Solubility of carbon in silicon and germanium, J. Chem. Phys. 30 (6) (1959) 1551–1555.
[11] B.M. Turovskii, I.I. Ivanova, Temperature dependence of the viscosity of fused silicon, Inorg. Mater. 10 (12) (1974) 1809–1812.
[12] W.P. Minnear, Interfacial energies in the Si/SiC system and the Si + C reaction, Commun. Am. Ceram. Soc. (1982) C10–C11.
[13] H. Zhou, R.N. Singh, Kinetics model for growth of silicon carbide by the reaction of liquid silicon with carbon, J. Am. Ceram. Soc. 78 (9) (1995) 2456–2462.
[14] J.N. Ness, T.F. Page, Microstructural evolution in reaction-bonded silicon carbide, J. Mater. Sci. 21 (1986) 1377–1397.
[15] R. Pampuch, J. Bialoskorski, E. Walasek, Mechanism of reactions in the $Si_l + C_f$ system and the self-propagating high-temperature synthesis of silicon carbide, Ceram. Int. 13 (1987) 63–68.
[16] M. Singh, D.R. Behrendt, Reactive melt infiltration of silicon–molybdenum alloys into microporous carbon performs, Mater. Sci. Eng. A194 (1995) 193–200.
[17] M.H. Hon, R.F. Davis, Self-diffusion of ^{30}Si in polycrystalline β-SiC, J. Mater. Sci. 15 (1980) 2073–2080.
[18] M.H. Hon, R.F. Davis, Self-diffusion of ^{14}C in polycrystalline β-SiC, J. Mater. Sci. 14 (1979) 2411–2421.
[19] R. Deike, K. Schwerdtfeger, Reactions between liquid silicon and different refractory materials, J. Electrochem. Soc. 142 (2) (1995) 609–614.
[20] H. Robbins, B. Schwartz, Chemical etching of silicon, J. Electrochem. Soc. 106 (6) (1959) 505–508.
[21] D.R. Turner, On the mechanism of chemically etching germanium and silicon, J. Elecrochem. Soc. 107 (10) (1960) 810–816.
[22] W.B. Hillig, Making ceramic composites by melt infiltration, Am. Ceram. Soc. Bull. 73 (4) (1994) 56–62.
[23] V.L. Yupko, G.G. Gnesin, Contact reaction of silicon carbide with liquid silicon, Soviet Powder Metall. Metal Ceram. 10 (130) (1973) 856–859.
[24] S. Hauttmann, T. Kunze, J. Muller, SiC formation and influence on the morphology of polycrystalline silicon thin films on graphite substrates produced by zone melting recrystallization, Thin Solid Films 326 (1–2) (1998) 175–179.
[25] K. Yanaba, M. Akasaka, M. Takeuchi, M. Watanabe, T. Narushima, Y. Iguchi, Solubility of carbon in liquid silicon equilibrated with silicon carbide, Mater. Trans.—JIM 38 (11) (1997) 990–994.
[26] O. Paccaud, A. Derré, Silicon carbide coating for carbon materials produced by pack cementation process, J. Phys. IV C5 (1995) 135–142.
[27] P. Pascal, in: P. Pascal (Ed.), Nouveau traité de chimie minérale, tome VIII, Masson, Paris, 1965.
[28] G.G. Gnesin, A.V. Kurdyumov, The Importance of the State of Aggregation of Silicon during Siliconization and the Nature of the Silicon Phase in Siliconized Graphite, Silicon Carbide, IN Frantsevich, New York, 1970.
[29] T. Birkel, Etude de la Corrosion des Matériaux Carbonés par l'aluminium Liquide et ses Alliages, Thèse de l'Université de Nancy I, 1994.