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Synthesis of silicon carbide whiskers using the vapour–liquid–solid mechanism in a silicon-rich droplet

T. BELMONTE, L. BONNETAIN, J. L. GINOUX
*Laboratoire Science des Surfaces et Matériaux Carbonés, URA CNRS 413, INPG, Ecole Nationale Supérieure d'Electrochimie et d'Electrométallurgie de Grenoble, Domaine Universitaire, 1130 Rue de la Piscine, 38402 St-Martin d'Hères Cedex, France**

SiC whiskers can be produced from 1350–1500 °C by carbothermal reduction of the silica in a fixed bed percolated by a hydrogen flow. At 1450 °C and above, the addition of iron to the silica–carbon mixture leads to the formation of submicrometre whiskers in the bed, ending with a silicon-rich droplet. The iron has evaporated and condensed at a lower temperature, a few centimetres downstream from the bed, allowing the formation of silicon carbide whiskers ending with an iron droplet according to the vapour–liquid–solid (VLS) mechanism. Submicrometre whiskers are also obtained without iron over a broader range of temperatures. Silicon carbide whisker production in a fixed bed is then possible using a (VLS) mechanism in a silicon-rich droplet and may be controlled without the addition of transition metals, thus improving the purity.

1. Introduction

The vapour–liquid–solid (VLS) mechanism was introduced by Wagner and Ellis [1]. For SiC whiskers, silicon and carbon may be provided by the gas phase as SiO and CH_4 forms [2]. Both elements, dissolved in the liquid phase, precipitate as SiC whisker. Such a mechanism is easily identifiable as the whiskers end with a solidified droplet. Therefore, this type of growth has led to a synthesis processes where the liquid droplet is obtained by adding catalytic impurities (often transition metals) capable of dissolving carbon and silicon [3–5].

Recently, it has been shown that the VLS mechanism can involve a silicon-based [6] droplet: in the growth of silicon oxycarbide whiskers, dissolution seems to occur in an amorphous SiO droplet. The existence of the amorphous SiO species is debatable [7, 8], notably because of the inaccuracy of its free standard formation enthalpy

$$Si + SiO_2 \rightarrow 2SiO_{amorphous}$$

$$\Delta G^f(1300\,^\circ C) = -11 \pm 17\ kJ\ mol^{-1} \quad (1)$$

Moreover, in their study on silicon carbide whiskers grown from rice hulls, Lee and Cutler [9] set out a growth mechanism in which a silicon liquid phase is involved according to the following reactions

$$SiO + C \rightarrow Si_{liq} + CO \quad (2)$$

$$Si_{liq} + C \rightarrow SiC \quad (3)$$

The major interest of this means of producing SiC whiskers is that they only contain carbon and silicon, and thus have improved purity.

The aim of the present work was to show that the growth of silicon carbide whiskers using the VLS mechanism in a silicon-rich droplet is now controlled and can be reproduced under very drastic conditions. The nature of the liquid phase and the morphology of whiskers will be discussed.

2. Experimental procedure

SiC whiskers were produced by silica carbothermal reduction under a hydrogen flow, according to the overall equation

$$3C + SiO_2 \rightarrow SiC + 2CO \quad (4)$$

Synthesis was performed in a fixed bed percolated by a $10^{-5}\ m^3\ s^{-1}$ at STP hydrogen vertical flow in a graphite furnace (0.08 m diameter). A graphite grid held the powder mixture (silica 57 wt %, carbon 43 wt %) where the carbon content was in excess with respect to stoichiometry. The powders silica Aerosil 380 and carbon FW2 from Degussa were chosen in very pure form to avoid the catalytic effect of uncontrolled impurities: the impurity content (CaO, Na_2O, etc.) is guaranted lower than 0.2 wt %. The particle diameter for carbon and BET surface area were respectively 13 nm and $516\ m^2g^{-1}$, and 7 nm and $380\ m^2g^{-1}$ for silica [10]. The mixture was prepared in a rotary mixer (10 min rotation at $3\ rad\ s^{-1}$). The

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density of the mixture was initially 75 kg m^{-3}. Iron was added to the powder mixture as solid $FeCl_3$, and reduced by hydrogen at 600 °C for 24 h in a specific oven before loading in the graphite furnace. The powders mixed without iron and those before and after reduction of iron when it was added, were observed by scanning electron microscopy. Whatever the mixture, carbon–silica agglomerates were observed with an average diameter of 10 μm and open porosity. Particles of iron, when introduced, were found to be lying on the agglomerate surface with an average diameter of 1 μm.

The furnace rise was set to 13 K min^{-1}. A constant temperature was maintained for 6 h. CO evolution was then near zero. Because of an axial temperature gradient, the temperature was 50 K lower 10 cm downstream from the bed but the bed was at a uniform temperature. The SiC weight yield was determined by elementary analysis of the output after burning out excess carbon in air at 600 °C for 2 h.

3. Results

Experiments under inert gas (argon and helium) under various conditions of temperature and flow rate, were carried out without iron addition [10, 11]. No whiskers but particles were obtained. With iron, whiskers were clearly produced, so the reactive powders have no catalytic impurities.

In the absence of iron and using hydrogen as gas flow, higher SiC weight yields were achieved, reaching nearly 100% at 1500 °C and above (Fig. 1). Only spherical particles were obtained at 1550 °C, but below this temperature whiskers were produced in the bed.

Whiskers obtained without iron were cylindrical. Their average diameter was just under 1 μm with a small dispersion around this value. X-ray analysis showed the dispersion to be β-SiC. STEM studies have indicated neither inclusions nor closed pores in the core of the whiskers.

Scanning electron microscope observations show clearly that the tip of the whiskers is usually ellipsoidal (Fig. 2). An X-ray micro-analysis of the tip reveals no other element than silicon with atomic number greater than 10. The concentration of light elements such as oxygen or carbon in the droplet could not be quantified, because of its small diameter. So, we can conclude that the droplet could either be Si, SiO or SiO_2 with some carbon supposed to be also present in the droplet. This implies that the whiskers grow according to the VLS process. This will be discussed further.

For mixtures containing 1 wt % iron, and flushed by hydrogen, the SiC weight yield was also plotted versus temperature (Fig. 3). Up to 1450 °C, the yield with 1 wt % iron was nearly 10 % higher than the same without iron. Above 1450 °C, both curves merged together because the silica carbothermal reduction was almost complete.

Iron-rich droplets at the end of the whiskers could only be found below 1450 °C. Above this temperature, the whiskers changed in morphology (Fig. 4). They became more uniform and very straight, contrary to the twisted forms obtained below 1450 °C. X-ray micro-analysis of the whiskers produced above 1450 °C showed there was no iron in the end droplets, only silicon.

Thus, whiskers grown at 1500 °C in the fixed bed containing iron were similar to the whiskers grown from an iron-free mixture. The growth mechanism will be discussed later.

Simultaneously, in the bed's downstream zone, SiC whisker deposition was found on the furnace graphite wall. The whiskers had obviously grown according to the VLS mechanism because they ended with iron-rich droplets (Fig. 4). So, the latter whiskers were obtained by chemical vapour deposition; the catalyst iron was also brought by the gas flow from the bed on to the furnace's inner graphite surface where it condensed and allowed silicon carbide whiskers to precipitate. The distance between the reaction bed and the SiC deposition zone changed with the bed temperature (between 1 cm at 1500 °C and 10 cm at 1550 °C) but this deposition always occurred at 1500 °C.

Whiskers produced in the downstream zone had an average diameter around 10 μm. Iron droplets at the end of the whiskers had a much larger diameter. They were studied using the Castaing micro-probe (WDS). Two distinct areas were found, the atomic compositions of which were

light area: Fe 63 at %; Si 37 at %; C traces.

dark area: Fe 72.5 at %; Si 27.5 at %; C traces.

These characterizations prove the existence of a binary compound near of Fe_3Si–Fe_5Si_3 suggested by Bootsma *et al.* [5].

4. Discussion

4.1. Iron transport

Above 1450 °C, 1 wt % iron mixed with the reaction powder was evaporated under the experimental conditions given above. This transport of iron is linked to two parameters: the presence of hydrogen (no evaporation is found when hydrogen is replaced by helium or nitrogen [10]), and temperature.

Gaseous compounds of iron, liable to be formed in the Fe–SiO_2–C–H_2 system, are few. $Fe(CO)_5$ is too unstable at this temperature, and thermodynamic calculations have clearly shown that the FeH_2O_2 partial pressure is negligible ($< 10^{-10}$ atm) in comparison with the iron vapour partial pressure. So, the iron vapour should be responsible for iron transport. Iron condensation in lower temperature zones gives liquid droplets which become catalytic agent in the (VLS) synthesis of SiC whiskers. The large diameter of the droplets may be connected to the non-wettability of graphite by pure iron [11] or because iron is continuously brought by the gas phase to the droplet.

The part played by hydrogen in this phenomenon should be to increase the gaseous iron partial pressure above the liquid phase by its decarburization: at 1500 °C, the iron equilibrium pressure changes from 0.59 Pa to 3 Pa. The gas flow nature could then explain iron transport.

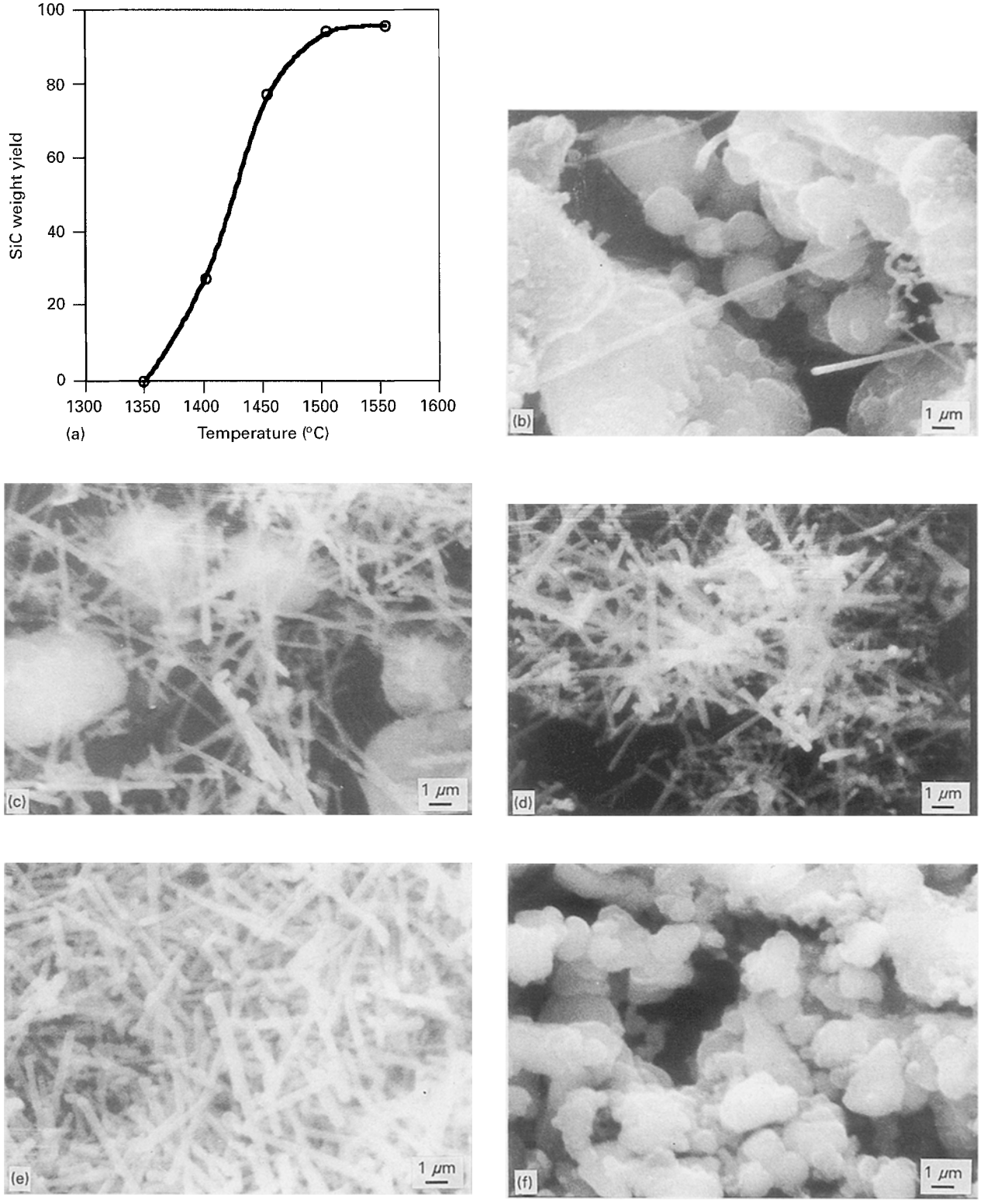


Figure 1 (a) SiC weight yield versus temperature. The initial mixture contains no iron. (b–f) The microstructure at (b) 1350 °C, (c) 1400 °C, (d) 1450 °C, (e) 1500 °C, and (f) 1550 °C.

This deposition in the bed's downstream zone produces effects comparable to those obtained by Milewski *et al.* [2] (Los Alamos process), although iron here is not initially painted on the wall but continuously brought by the gas phase.

4.2. Growth mechanism

Whiskers with iron-free droplets (Fig. 2) are obtained between 1400 and 1500 °C from iron-free mixtures and between 1450 and 1500 °C from mixtures with 1 wt % iron, because vaporization of iron occurs mainly above 1450 °C. Whatever the iron concentration, the whisker growth mechanism is the same and involves the pure silicon or silicon-rich droplet. In the latter case, the droplets at the tip are ellipsoidal whereas they are generally spherical when containing the usual transition metals. Moreover, the inequality proposed by Bootsma *et al.* [5] for the VLS mechanism, i.e. $1 <$ droplet diameter/whisker diameter < 1.5, is observed.

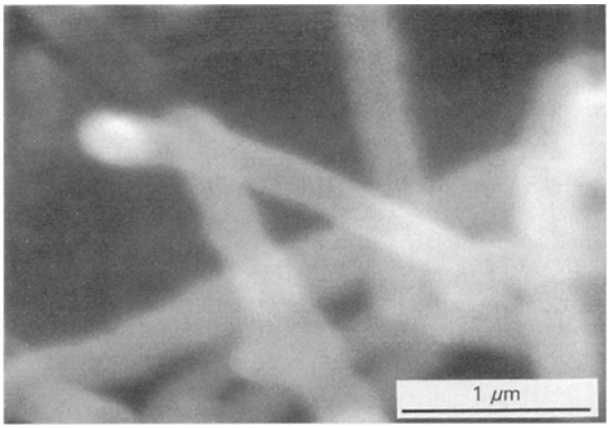


Figure 2 Micrographs of a SiC whisker obtained without iron, ending in a droplet rich in silicon.

The growth mechanism without iron does not occur below 1400 °C, contrary to that with iron, so a greater activation energy should be required. This is consistent with the catalytic effect of iron.

The presence of a droplet at the tip of the iron-free whiskers and the transition to spherical SiC particles in the bed above 1550 °C, must now be explained.

As no inclusion was found in the core of the whisker produced without iron, the growth mechanism is probably not that described by Nutt [13] which implies the condensation from the gas phase of impurities on to the whisker and subsequently inclusions in the whisker core.

A growth on a screw dislocation such as that described by Sears [14] is debatable because the presence of a droplet at the end of each whisker is unexpected in such a mechanism and the whisker–particle transition at 1500 °C is hard to justify.

Let us consider now the VLS mechanism. Pure silicon melts at 1400 °C. The silicon-rich droplet could play the same role as the iron and then behave as a solvent of carbon, like transition metals. This mechanism is probably comparable with that suggested by Lee and Cutler [9].

Pure $SiO_2 + C$ mixture is thermodynamically unstable at atmospheric pressure in this range of temperatures. If the droplet is supposed to be SiO_2, it must be covered by a SiC pellet because of the presence of carbon. The carbon diffusion coefficient through SiC is $10^{-13}\,m^2\,s^{-1}$ in the grain boundary and $3.7 \times 10^{-17}\,m^2\,s^{-1}$ in a crystal [15]. In all cases, carbon (and probably silicon too) diffusion through the

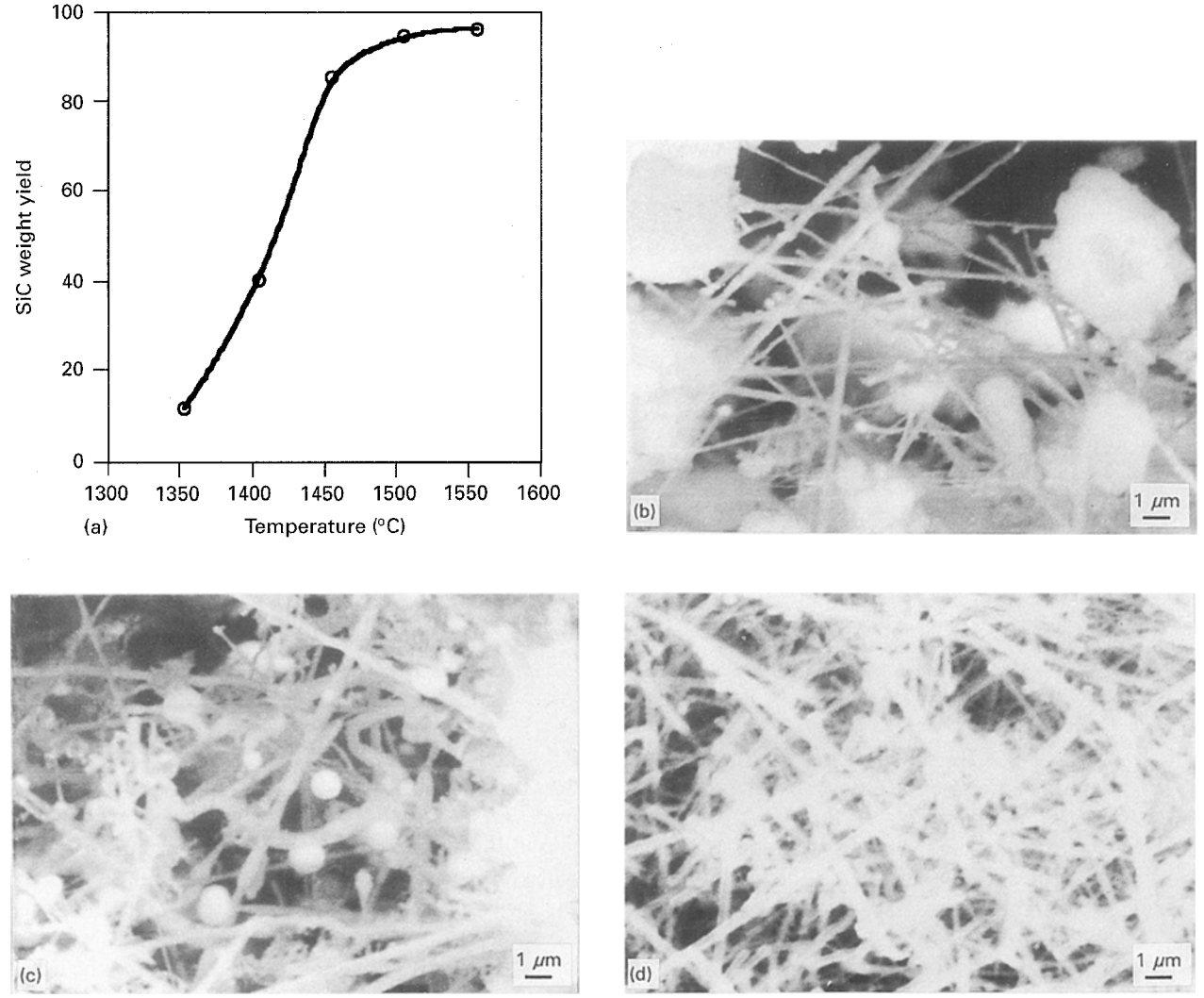
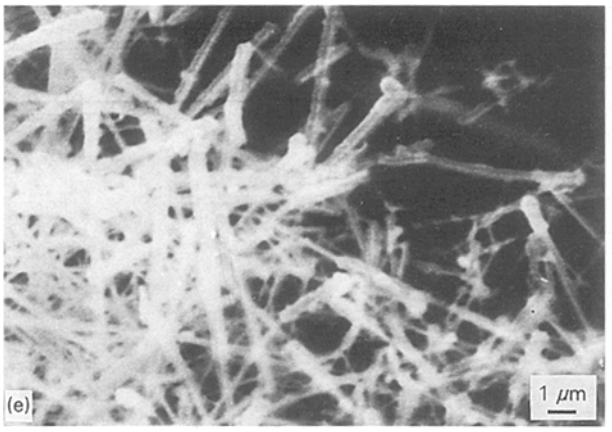


Figure 3 (a) SiC weight yield as a function of temperature. The initial mixture contains 1 wt % iron. (b–f) The microstructure at (b) 1350 °C, (c) 1400 °C, (d) 1450 °C, (e) 1550 °C, and (f) 1550 °C.



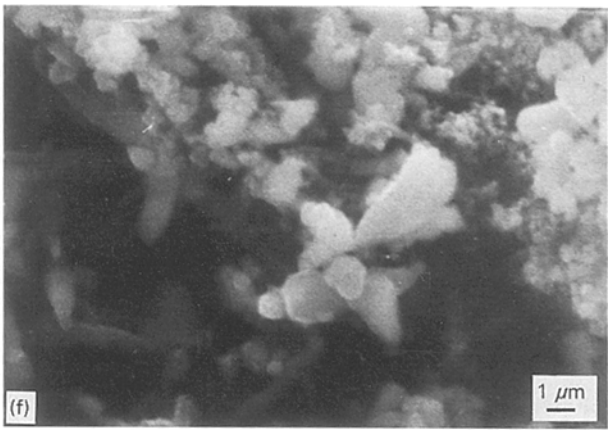


Figure 3 (continued)

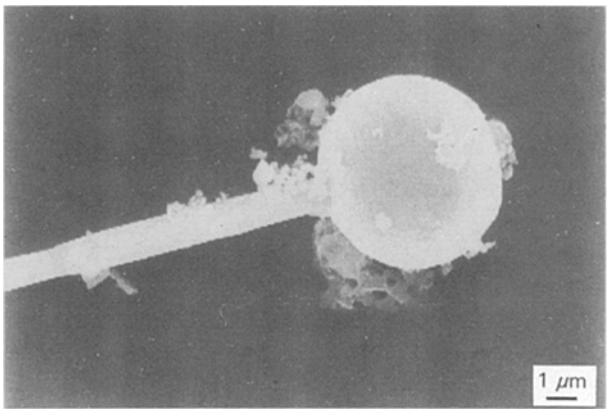


Figure 4 Micrographs of SiC whiskers produced in the downstream zone.

SiC pellet too slowly to ensure whisker growth for the treatment time used, and this assumption must certainly be dismissed.

It is not yet well known if amorphous SiO can be distinguished from an Si–SiO_2 mixture. Despite little differences in physical and thermodynamic properties between condensed SiO and the Si–SiO_2 mixture, Rocabois [16] has established that the former is a mixture of micro-domains of silicon and SiO_2. According to Rocabois observations, it is possible to suppose that condensed SiO would behave like a Si–SiO_2 mixture. Then, the discussion for the growth mechanism is the same as that for silicon and SiO_2.

If the role of hydrogen on iron vapourization is almost clear, it is essential to define what influence it can have on the droplet. The quaternary system to be considered here is Si–O–C–H, and little is known about it. To explain the appearance of SiC particles at 1550 °C, a thermal destabilization of the silicon-rich droplet must be looked for at this temperature, either because of the decarburization of the silicon-rich droplet as for the iron droplet, or simply because of the temperature elevation effect.

Furthermore, hydrogen certainly has an influence on the growth itself. No whiskers have been obtained under the same experimental conditions with non-hydrogeneous gas [10, 11], such as helium or argon. Without hydrogen, the droplet is only provided via carbon by CO, whereas it is essentially via CH_4 with hydrogen. In the latter case, carbon dissolution is known to be easier, and this could explain the suggested growth of whiskers in a silicon-rich droplet under a hydrogen flow.

In conclusion, the VLS mechanism in a silicon-rich droplet (either silicon or SiO_2 or a mixture of both) could explain the presence of the droplet and the whisker–particle transition above 1550 °C. Because of the lack of information on the composition of the droplet, many steps in the general mechanism remain hypothetical and must be clarified.

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