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ON THE SYNTHESIS OF SiC SINGLE CRYSTALS

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5 September 1972

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On the Synthesis of SiC Single Crystals
SiC 単 結 晶 の 作 成 方 法

YOSHIZO INOMATA 猪 股 吉 三
HIROKICHI TANAKA 田 中 広 吉

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13. ABSTRACT

A method is proposed to synthesize SiC single crystals free of carbon particle inclusions. An empty graphite crucible is connected with the crucible containing silicon melt by means of a graphite pipe. The former crucible is heated to approximately 2,500°C, as in the ordinary sublimation process, while the temperature of the latter is lowered. Crystal growth is accomplished in the empty crucible. The experiments conducted are preliminary. Problems such as damages to the crucible containing silicon melt, prevention of silicon leak, and control of the amount of silicon supply to the growth cavity are examined. The structure of the furnace necessary for the implementation of the method is also discussed.

Details of illustrations in
this document may be better
studied on microfiche.

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On the Synthesis of SiC Single Crystals

1. INTRODUCTION

Thus far, large SiC single crystals have been synthesized using mainly the technique of sublimation and recrystallization (Addamiano et al, 1963; Hamilton, 1958; Inomata et al, 1968; Knippenberg, 1963; Kroko, 1966: Lely, 1955). The technique, however, tends to allow the grown crystals to contain minute carbon particles due to the process under a carbon-rich atmosphere (Inomata et al, 1970). The problem can be solved if silicon vapor can be supplied into the growth cavity.

The greatest difficulty in this attempt is to safely maintain the molten silicon at temperatures above 2,000°C. In this paper a method is proposed to sustain a higher silicon vapor pressure inside the growth cavity than that in the normal sublimation process; the feasibility of the method is investigated based on experimental facts.

While experimentation is still in progress (having been hindered by the use of a high-temperature furnace inadequate to attain the full objective), this paper is published for the purpose of presenting preliminary findings to those who are interested in the field of SiC crystal growth.

2. PROPOSAL OF A NEW METHOD OF CRYSTAL GROWTH

The reaction system used is schematically shown in Figure 1, with (4) representing the growth cavity, (6) the crucible to hold molten silicon, and (5) a pipe to

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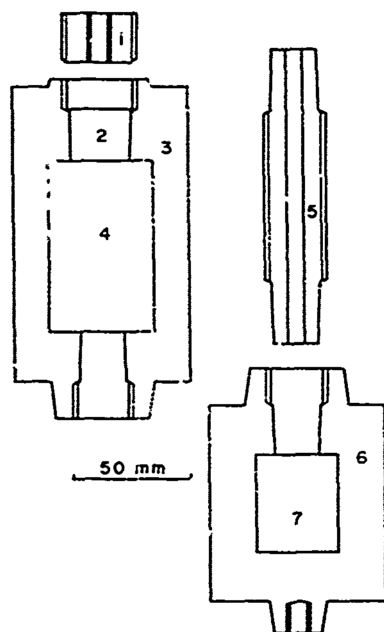

Figure 1. A Scheme for Growth Cavity Construction. (1) Screw; (2) tapered plug; (3) crucible; (4) growth cavity; (5) screwed pipe tapered at both ends; (6) crucible; (7) cavity for Si melt

connect crucibles (3) and (6) by threading and tapering. A radiation shield is attached to (5) to maintain the desired temperature difference between the solvent silicon and the growth cavity.

Control of the amount of silicon supplied into the growth cavity is accomplished by adjusting the diameter and length of pipe (5), the diameter and length of the graphite diffusion baffle enclosed in this pipe, and the number of radiation shields attached to the pipe.

Since the method calls for uniform heating of the entire reaction system as the temperature passes through the melting point of silicon, use of a furnace equipped with two separately controllable graphite heaters is desired. Degassing of the hermetically sealed crucible is difficult. However, the problem can be alleviated by designing a furnace where the crucible can be heated in a vacuum up to approximately 1, 300°C as it is degassed, argon is introduced, the connecting part is closed, and heating is continued. This is possible since the section for the opening can be attached or detached below 1, 400°C.

Crystallization is carried out, as in the sublimation process, by heating the outer wall of the central portion of the growth cavity up to 2, 500°C. During crystal growth, silicon vapor from the melt is supplied into the growth cavity through the pipe and carbon is provided from the inner wall of the cavity.

3. INVESTIGATION OF FEASIBILITIES

3.1 Damages to the Graphite Crucible

Damages to the graphite crucible often occur during heating of silicon in the neighborhood of the melting point. This happens more frequently when the heating is performed in a vacuum or when there is a large temperature gradient in the crucible and the heating is carried out slowly in the neighborhood of 1, 400°C. These experimental facts show that in many cases the conditions under which damages

occur appear to be related to the amount of solidified silicon contained in the crucible during heating. This idea can be confirmed by investigating the results of employing conditions opposite to those mentioned above. Using fine graphite as raw material helps attain this goal. However, gradual melting of silicon at the temperature just above the melting point is difficult even when this material is used.

3.2 Silicon Leak From a Graphite Crucible

Use of material similar to that employed for the slowing-down of atomic piles, results in a high degree of permeation of molten silicon above 1,500°C. Therefore, given a crucible wall of 10 mm in thickness, silicon will seep through it and prolonged experiments will not be possible. At times the furnace is also liable to damage.

To prevent this, use of high-density (bulk specific gravity > 1.80), fine graphite material is recommended. Good results were obtained by using S. D. H. manufactured by the Nippon Carbon Co. Ltd., which had been purified before the experiment.

Let us consider leakage from the slit between the cover and the body of the crucible. Since silicon wets graphite well, normal fitting cannot prevent the leakage, making a long experiment above 2,000°C nearly impossible. Tapering the cover and the body helps prevent this leakage and works almost perfectly.

Figure 2 shows schematically a crucible for testing such fitting. Fit between the plug and the body is accomplished by a taper of 1/20 to 1/30.

The crucible was tested in the following manner: It is charged with 30 grams of silicon; the plug was pressure-fitted, and the entire crucible was placed into another graphite container with an outer diameter 80 mm and depth 100 mm which in turn was placed in the furnace. The system was heated up to 1,300°C in a vacuum, and after argon was introduced, it was heated further and held at 2,500°C for 2 hours. Following this process, hardly any silicon leak was observed.

Observation of the cross-section of the crucible following the experiment showed that the taper-fitted portions had uniformly turned into SiC, forming closely fitted structure SiC as thick as 4 mm formed on the inner wall of the graphite crucible. This led us to believe that SiC formed by the reaction between the silicon (which had permeated into the wall) and the graphite contributed to the prevention of silicon leak.

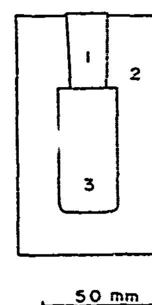

Figure 2. Graphite Crucible for Molten Si at 2,500°C. (1) Tapered plug; (2) crucible; (3) cavity

The above procedure is quite effective. For example, the boiling point of silicon is approximately 2,300°C (Chemistry Handbook, 1958), and the vapor pressure in the neighborhood of 2,500°C is estimated to be 10 kg/cm^2.

3.3 Formation of Single Crystals

Experiments were performed by direct insertion of the large reaction system described in Section 2 into a high-temperature furnace which the present experimenters had been using. However, since the temperature gradient within the furnace was large and the damages to the lower section of the crucible occurred frequently (by the same causes described in Section 3.1), an attempt was then made to carry out the process by using a crucible schematically shown in Figure 3.

The space between plug (3) and the opening of the crucible is taper-fitted. Screw (1) helps to pressure-close the plug into the crucible. The mid-section of (1) is tapped to permit the entire assembly to be suspended from the top. Radiation shield (5) is used for thermal insulation, that is, for maintaining the crystal temperature in the crucible. After placing approximately 40 grams of silicon in container (6), crystal growth proceeded under the condition that the temperature of the bottom section of (6) be approximately 200°C lower than the outer wall of the mid-section of growth cavity (4).

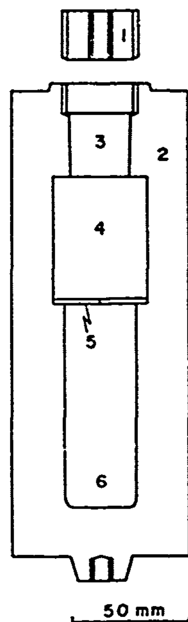

Figure 3. Graphite Crucible for Crystal Growth Experiments. (1) Screw; (2) crucible; (3) tapered plug; (4) growth cavity; (5) radiation shield split into two pieces; (6) molten Si container

The furnace had been evacuated overnight in advance to insure a vacuum of better than 10^{-5} Torr. Rotation of the crucible was at the rate of 2 rpm. The temperature was raised to 1,300°C in a vacuum of 10^{-5}-10^{-4} Torr, and argon of one atmospheric pressure was introduced at this temperature. The temperature was raised at 50°C/min in the neighborhood of the silicon melting point. The outer wall of the growth cavity was maintained at 2,400°C for 6 hours, and then the assembly was allowed to cool after the power had been turned off.

The crucible was removed from the furnace after cooling. Appropriate parts were cut off using a diamond cutter. Silicon that had adhered to the growth cavity was removed by a mixture of 1:1 nitric

acid and hydrofluoric acid. The crystals were then collected. Figure 4 shows the manner in which the crystals grew, as viewed from the top of the growth cavity. It is evident that they grew from the inner wall, just as in the sublimation process. Crystal adhesion to the wall was weak. Hardly any silicon leak was observed in the experiment.

3.4 Grown Crystals

Figure 5 is a dark-field photomigrograph of two α-type crystals grown at 2, 400°C for 6 hours, as described in Section 3. 3. The bright dots are voids which usually have openings at the crystal surface and often contain silicon. A few small ones were found free of silicon.

The crystal shown in Figure 6 was obtained without using a radiation shield. Because of the rapid cooling process, the crystal is coarse with a large silicon content and a rough base. None of the crystals obtained have carbon particle inclusions. From the facts described in Section 3. 3 and the present section, we see that the crystals grew while they were being cooled mainly by radiation as in the sublimation process. However, after cooling, the crystal surface and the inner wall of the growth cavity appeared to have been plated with silicon vapor. Based on the manner in which silicon was absorbed, it is natural to conclude that the crystal surface was wet with silicon during growth.

That is to say, even though the transition paths of the materials and heat were different, the growth process was exactly the same as that which involves solvent silicon. A deviation from the stoichiometric ratio between Si and C occurring in the crystal at a rate which poses a serious prbolem is undesirable. This will be discussed in the next section.

3.5 Control of the Amount of Silicon Supply

It was initially believed that in the method described in Section 3. 3 silicon was supplied into the growth cavity in the vapor phase from the surface of the molten silicon. However, if this were the case, the wetness mentioned above would not have occurred. That is, if the crystals on the inner wall of the growth cavity were wet with silicon, the vapor flow would have been directed downward from the growth cavity to the melt.

Thus, in the case of Section 3. 3 silicon must have been supplied into the growth cavity in the liquid phase with the aid of the wetness of the pipe wall. The cause of this must have been that the vapor pressure within the container was high and the diffusion speed of the silicon vapor was low compared with the supply speed through the wetness.

Figure 4. Growth Cavity After Elimination of Si

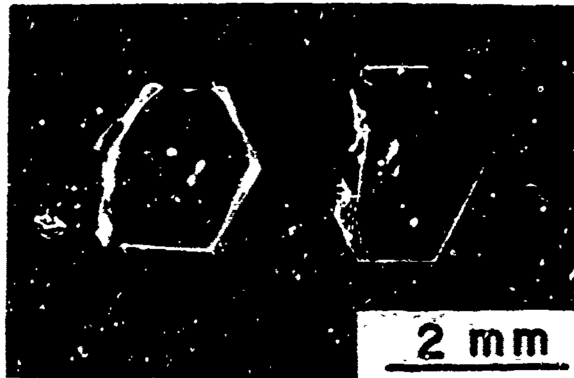

Figure 5. Dark-Field Photomicrograph of Crystals Grown at 2,400°C for 6 Hours

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Figure 6. A Large Crystal Grown Without Using a Radiation Shield. The dark portions are Si-containing voids

To attain the initial goal of controlling the amount of silicon supply, this wetness must be considered. The problem discussed in Section 3.3 can probably be solved because control of the amount of silicon supply is possible by the technique described in Section 2, that is, by adjusting the diameter and length of the pipe, the magnitude of the diffusion baffle, or the difference between the temperatures of the growth cavity and the molten silicon.

4. SUMMARY

SiC crystals were grown from a silicon-rich vapor phase under temperatures similar to those used in the sublimation process. A method was proposed to obtain crystals without carbon particle inclusions. The feasibility of the method was studied based on preliminary experimental data.

The graphite crucible containing molten silicon was connected with an empty graphite crucible by means of a pipe made of the same material. Crystal growth was accomplished by heating the latter crucible to approximately 2,500°C.

Problems such as damages to the crucible containing silicon melt, prevention of silicon leak, and control of the amount of silicon supply were examined. It was concluded that the proposed method is viable. The structure of the furnace necessary for the fulfillment of the method was also discussed.

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