

Mechanism of production of ultra-fine silicon carbide powder by arc plasma irradiation of silicon bulk in methane-based atmospheres

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The mechanism of production of ultra-fine SiC powder from a silicon bulk by arc plasma irradiation in either an Ar + CH₄ + H₂ or an Ar + CH₄ atmosphere was studied. Layer and island phases were newly formed in the silicon bulk upon irradiation, and it was revealed from scanning electron and Auger electron spectroscopy that these phases were composed of SiC. The intensity of the X-ray diffraction peaks due to the SiC phase increased with irradiation time almost in parallel to the carbon content involved in the silicon bulk. It is proposed that CH₄ is dissociated in the arc plasma and dissolved in the molten silicon bulk to produce the SiC phase, the sublimation of which is mostly responsible for the production of ultra-fine SiC powder.

1. Introduction

Ultra-fine powder is a potentially interesting substance both in fundamental research and in its technological use. For the production of ultra-fine metal powder, the arc plasma method was first employed by Uda [1, 2]. In our work, the efficient production of silicon powder, a few tenths of nanometre in size, was established by the arc plasma method [3], and the two-step production of silicon nitride by the gas nitriding of the silicon powder produced was also examined [4]. It is expected that the arc-plasma generation in a reactive atmosphere will lead to the production of two-component, or possibly more, non-metal compounds with high melting points. In this regard, our attention has been focused on the availability of the arc-plasma technique for the direct production of ultra-fine ceramic powder. Recently, we have reported a procedure for the direct production of ultra-fine Si₃N₄ powder using the arc plasma irradiation of a silicon bulk in an NH₃ atmosphere [5].

In view of the high hardness, high thermal conductivity, high-temperature resistance and chemical stability, of silicon carbide, the production of its ultra-fine powder has been recently attempted in several ways. Hollabough *et al.* [6] studied the r.f. plasma-inducing gaseous reactions between silane and methane, and Uda and Ohno [7] applied the arc plasma method to a bulk SiC in a hydrogen atmosphere. We have also made a preliminary examination of the direct production of ultra-fine SiC powder from a silicon bulk by arc plasma application in CH₄-based atmospheres [5]. This direct production of SiC powder by the arc plasma irradiation is of interest, but its formation process has remained ambiguous so far.

The present study was undertaken to reveal the mechanism of production of the ultra-fine SiC powder.

The powder produced was characterized by X-ray diffraction and electron microscopy. The structures and composition of the silicon bulk after arc plasma irradiation were analysed by X-ray diffraction, optical microscopy electron probe micro analysis (EPMA) and Auger electron spectroscopy (AES).

2. Experimental procedures

A laboratory-made arc plasma furnace, which was the same as described previously [3, 5], was used for the preparation of SiC. Metallic silicon lump (4 g), 98.1 wt % in purity (C < 0.09 wt %, P < 0.01, Al < 0.92, S < 0.02, Fe < 0.62 and Ca < 0.1) was placed on a copper anode at a distance of ~5 mm from a tungsten cathode which was directed at an angle of 45° to the normal axis of the sample. The chamber was evacuated below 100 Pa, and then filled with a gas stream (a flow rate of 121 min⁻¹) consisting of either an Ar (90 vol %) + CH₄ (10 vol %) or a Ar (80 vol %) + CH₄ (10 vol %) + H₂ (10 vol %) mixture. The total pressure was maintained at about 0.1 MPa. The purity of these gases was better than 99.999% for argon and hydrogen and 99.9% for methane. The arc was generated at a current of 150 A. The ultra-fine powder produced was collected from the surrounding wall shield. The different means of collection was the vacuum-pump suction of the produced powder through a small nozzle which was placed as close as possible to the silicon bulk sample.

The X-ray diffraction patterns of the powder and bulk were recorded on a diffractometer, Rigaku Denki, Rad III. The micro-shape and crystal structures of the powder were monitored by a 200 kV electron microscope, Jeol, JEM 200CX. The EPMA and AES analyses of the chemical compositions for the small spots of the silicon bulk samples were performed

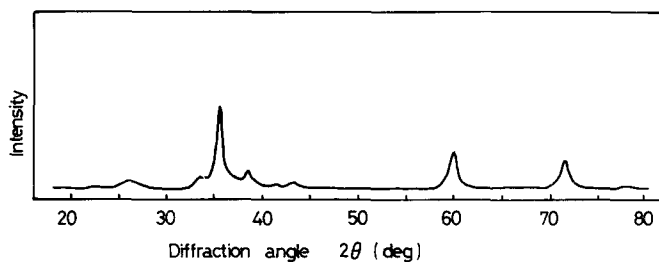


Figure 1 X-ray diffraction pattern of ultra-fine SiC powder. Gas mixture: 80% Ar, 10% CH₄ and 10% H₂.

with spectrometers Jeol JXA-733 and Jeol JAMP-10S, respectively.

3. Results

When a silicon lump was irradiated by the arc in either an Ar + CH₄ or Ar + CH₄ + H₂ atmosphere, the initial stage was its melting, followed by the generation of smoke externally from the surface of the molten silicon. The SiC powder produced contained impurities such as Cu (0.11 wt %), Fe (0.22), Al (1.6) and Ca (0.77). A small amount of copper probably results from the copper anode. The rest was the same impurities as those involved in the source silicon material; considerably higher contents of calcium and aluminium elements in the powder are evidently due to their easy evaporation.

Fig. 1 shows a typical X-ray diffraction pattern of the ultra-fine SiC powder produced in a mixture of Ar, CH₄ and H₂. Major peaks appear at around diffraction angles of 33.7°, 35.6°, 60.0° and 71.7°, together with smaller peaks at 41.3° and 43.1° (a peak at 38.5° is less reliable, because of the overlap with a peak from the underlying aluminium support). These peaks are associated with SiC. A peak of silicon at around 28° is small. Under the conditions of Ar (80 vol %) + CH₄ (10%) + H₂ (10%), the rate of SiC production was estimated to be approximately 1×10^{-4} mgJ⁻¹. For analysis of the SiC bulk subjected to similar arc-plasma irradiation, new X-ray diffraction peaks were found which grew with increasing irradiation time. As shown in Fig. 2, after 300 sec irradiation, the original silicon peaks at diffraction angles of 28.2°, 47.1° and 56.1° became extremely small, whereas the new peaks were clearly observed, for example, at around 33.8°, 35.4°, 59.9° and 71.5°.

In accordance with the previous results [5], the ultra-fine powder produced has nearly spherical structures, mostly with a particle size of 20 to 40 nm and hexagonal shapes 100 to 200 nm diameter. Unfortunately, the particle size distributions of SiC powder produced could not be determined from the electron microscopic observations, because it was difficult to distinguish the SiC particles from the amorphous carbon particles.

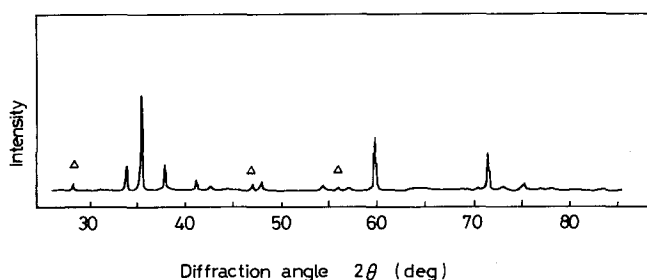


Figure 2 X-ray diffraction pattern of silicon bulk after arc plasma irradiation. Gas mixture: 80% Ar, 10% CH₄ and 10% H₂. Irradiation time, $t = 300$ sec. (Δ) Si.

The amount of carbon involved in the silicon bulk after the arc plasma irradiation in an Ar + CH₄ gas was monitored. Fig. 3 shows the change in carbon content with time of exposure to arc-plasma irradiation. The formation of carbon in the bulk silicon was initially slow but accelerated as the irradiation proceeded over 100 sec. Fig. 3 also shows the change in the intensity of X-ray diffraction SiC peak (35.4°) with irradiation time. It is to be noted that the peak grows in an almost similar way to the increase in carbon content involved in the silicon bulk.

After arc plasma irradiation, the bulk silicon lumps were cut into two pieces, and their sections were optically observed. Fig. 4 shows the cross-sectional view of the silicon bulk. One feature is that there exists a large number of voids of a few millimetres average size in the deep interior of the bulk and, in addition, heterogeneous microstructures such as layers and islands are clearly observed. It is interesting to see that the layer structures are formed near the surface along the direction of the arc plasma flame and that islands are distributed rather in the inner part of the bulk. The SEM image and EPMA analysis for the same spot demonstrated that one phase forming either islands or layers is rich in carbon, whereas the rest contains little carbon, as is shown in Fig. 5. The EPMA results seem to indicate the presence of elemental silicon in both the phases but its image contrast is not clear enough to exhibit the differences in the silicon distributions. Fig. 6 shows the results of AES microanalysis for the two phases. Both phases give rise to marked Si KLL (four peaks in 1560 to 1616 eV) and LMM (93 eV) Auger lines, whereas C KLL (273 eV) appears significantly at merely one phase with the island and layer structures. Thus, it is evident that both the layers and islands consist of SiC, while the surrounding matrix is a silicon phase.

4. Discussion

4.1. Silicon carbide powder

Silicon carbide is a typical compound with polytypism, and its basic polytypes with high formation probability are 2H, 3C, 4H, 6H and 15R (these are α -SiC except for 3C of β -SiC). In these structures, the first two SiC

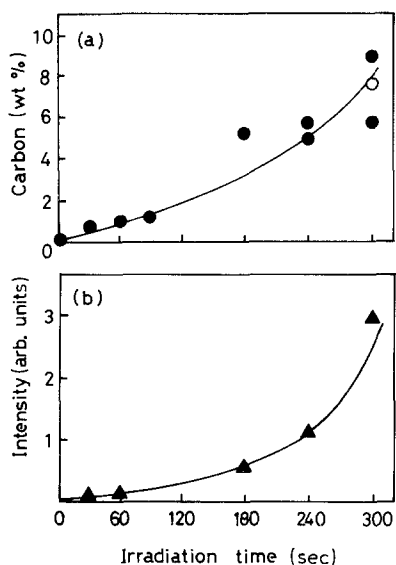
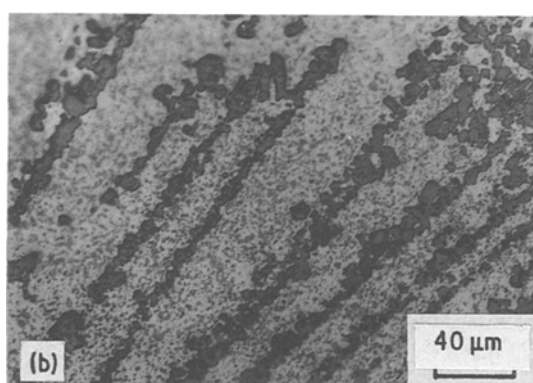
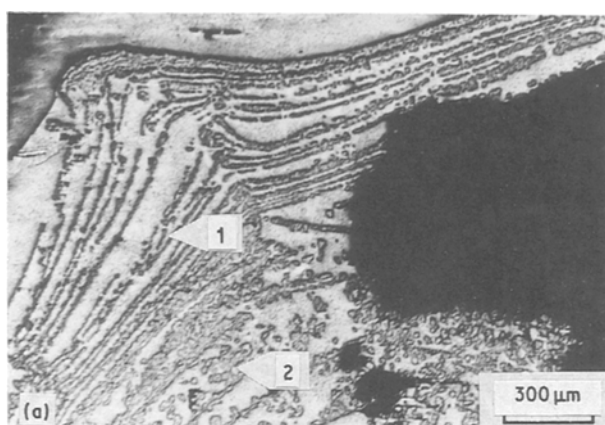


Figure 3 (a) Increase of carbon content in silicon bulk and (b) of X-ray diffraction peak, with arc plasma irradiation time. Gas mixture: (●) (▲) 90% Ar and 10% CH₄, (○) 80% Ar, 10% CH₄, and 10% H₂.

are usually observed below 1870 K, 4H is stable at around 2100 K and the others are favoured between 2500 and 2900 K [8–10]. As far as temperature is concerned, the formation of α -SiC is likely to proceed, because the temperature of silicon bulk in the arc plasma heating is estimated to be ~ 2500 K [3]. On the other hand, the conditions with excess silicon are inclined to produce β -SiC [11], and the present silicon-rich situation might favour the formation of β -SiC. The electron diffraction patterns were too complicated to determine the definite crystal structures, but in the

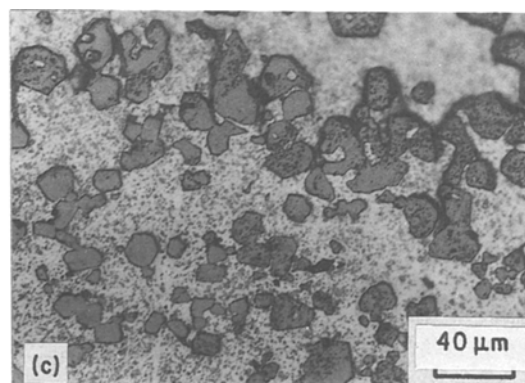


X-ray diffraction pattern, the presence of peaks around 33.7° , 41.3° and 43.1° , in addition to 35.6° , 60.0° and 71.7° , indicates that α -SiC with hexagonal structure is at least produced under the present conditions, although β -SiC also might be involved. In particular, the diffraction at 33.7° is characteristic of α -SiC with 4H and 15R structures. In a previous study [5], SiC powder produced from silicon bulk in a CH₄ + Ar atmosphere was assigned to β -SiC with cubic structure. The difference is the involvement of hydrogen in the present arc plasma gas, which evidently causes larger dissolution of hydrogen atoms in the molten silicon bulk. The increasing concentration of hydrogen results in its recombination to be desorbed as a gas phase, by which appreciable heat is liberated to the surrounding silicon matrix. This is in line with the interpretation proposed by Uda [1, 2] for the role of two-atom molecules in the arc plasma activation. Thus, it is plausible that the presence of hydrogen in the arc plasma atmosphere increases the temperature of the silicon bulk and hence leads to the favourable production of high-temperature stable α -SiC.

4.2. Process of ultra-fine SiC powder formation

The X-ray diffraction patterns of the arc plasma irradiated silicon lump resemble those of SiC powder and can be associated with α -SiC. The EPMA and AES analyses revealed that the SiC phases were distributed as layers and islands in the silicon bulk. The formation of SiC layers near the surface along the direction of the arc plasma flame, apparently results from the occurrence of convection in the molten silicon. These observations suggest that the first process in SiC powder production is the formation of SiC phases in the silicon bulk. The decomposition of CH₄ into CH₃ and CH₂ in the gas phase takes place, in the presence of argon, with an activation energy of 418 kJ mol^{-1} at temperatures higher than 1200 K [12, 13]. As mentioned above, the estimated temperature in the arc-plasma conditions is high enough to produce atomic hydrogen and carbon near the silicon surface. Furthermore, it is likely that the silicon surface itself functions as a catalyst on which the dissociation of CH₄ is promoted. Thus, melting of silicon

Figure 4 (a) Optical photomicrograph of a cross-sectional view of the silicon bulk after arc plasma irradiation. (b) and (c) Enlarged views of areas 1 and 2, respectively. Gas mixture: 90% Ar and 10% CH₄. Irradiation time, $t = 300$ sec.



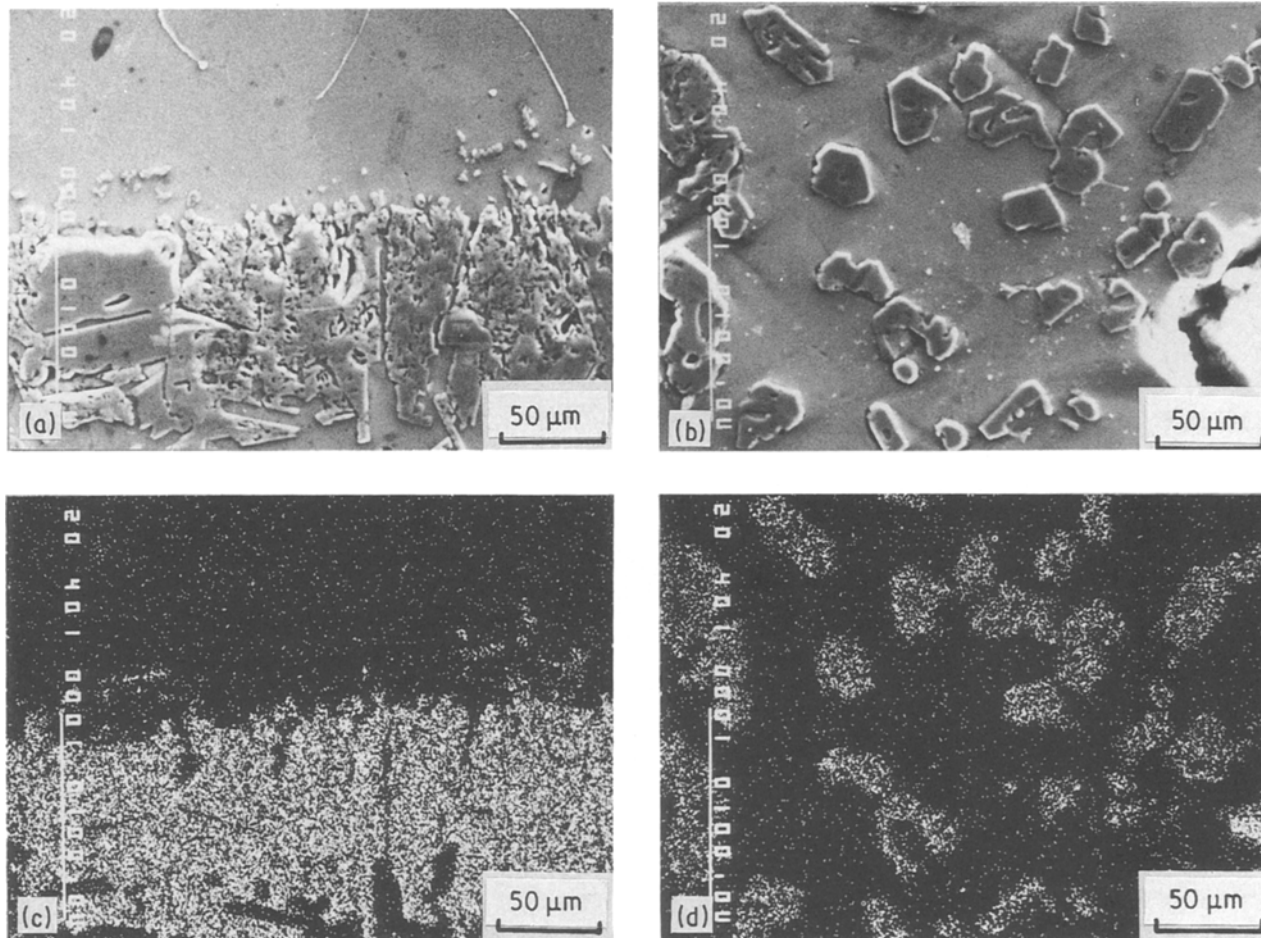


Figure 5 Layer and island structures produced in silicon bulk by arc plasma irradiation. (a, b) SEM images, (c, d) carbon distribution (white areas). Gas mixture: 90% Ar and 10% CH₄.

by the arc is readily followed by the dissolution of carbon and hydrogen atoms.

The Gibbs free energy of SiC formation from silicon and carbon is given by the equation

$$\Delta G = -53.4 + 6.95 \times 10^{-3} T \text{ kJ mol}^{-1}$$

where T is temperature [14]. Thus, the production of SiC is thermodynamically favoured for a temperature estimated as 2500 K for the arc plasma heated silicon bulk. Therefore, the dissolved carbon atoms can react with silicon atoms to produce SiC in the molten silicon bulk.

The flow due to convection in the molten bulk permits exposure of the SiC to the surface. We have observed that a large number voids is formed in the bulk after arc plasma irradiation, thus indicating the evolution of dissolved hydrogen as bubbles. This bubbling effect is also useful in bringing the SiC to the surface. Thus, it is reasonable to consider that the sublimation of the SiC produced is the major process in the production of ultra-fine SiC powder. The evaporated SiC probably coalesces in the gas phase near the surface. Because the sublimation temperature of SiC is about 2880 K, the close agreement in temperature between the arcplasma-treated silicon and its sublimation temperature offers suitable conditions for SiC powder formation.

Another mechanism which is different from the sublimation of SiC is the direct gas phase reaction

between evaporated silicon and CH₄. The contribution of this process to the powder production is not clear at present but seems small, because it is expected that the rapid reaction of the silicon bulk with CH₄ results in the preferable formation of surface SiC

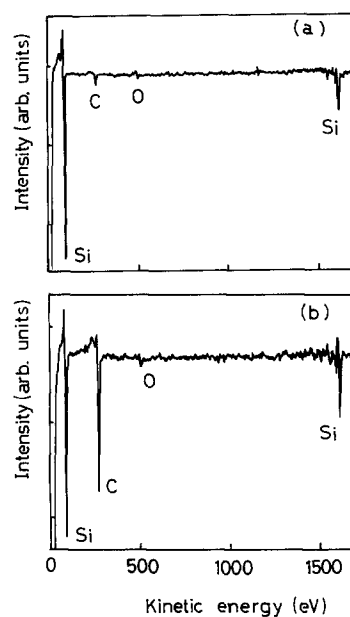


Figure 6 Auger electron spectra of silicon bulk after arc plasma irradiation. (a) Non-island phase and (b) island phase in the cross-section in Fig. 5. Each surface was etched prior to measurement by argon sputtering for 2 min.

layers, which prevents the evaporation of silicon atoms. Furthermore, in our preliminary work in which an SiC bulk involving 10 wt % Si is used as a starting material and irradiated by the arc in an Ar + H₂ atmosphere, a remarkable generation of ultra-fine SiC powder has been observed, which gives support to the present view that the sublimation of SiC phases is a major process. This situation is quite different from the case of Si₃N₄ formation by arc plasma irradiation of silicon bulk using NH₃ as one of reactant gases [5]. Because the temperature of Si₃N₄ decomposition is as low as 1573 to 1723 K for α -Si₃N₄ and 2073 K for β -Si₃N₄ [14], it is unlikely that ultra-fine Si₃N₄ powder is produced via evaporation following the formation of bulk Si₃N₄ phase. The absence of ultra-fine Si₃N₄ powder after arc plasma irradiation of Si₃N₄ bulk in an H₂ + Ar mixture is consistent with this view. These results suggest that a gas phase reaction between evaporated silicon and NH₃ is predominant for the formation of Si₃N₄ powder.

When the composition and structures of the silicon bulk were examined as a function of arc plasma irradiation time, a fairly good relationship was found between the increase in the carbon contents involved and the enhancement of the X-ray diffraction peak intensity of SiC. This suggests that most of the carbon is combined with silicon atoms to produce the SiC phase. As shown in Fig. 3, the carbon content in the silicon bulk was almost the same in the presence and absence of hydrogen in the arc plasma gas. Thus, it seems that the dissolved hydrogen has little influence on the formation of the SiC phase in the silicon bulk. This result also suggests that the formation of amorphous carbon in the powder is not due to the decomposition of SiC upon sublimation, but mostly to the direct plasma reaction between gaseous CH₄.

Thus, the previous findings that the amorphous carbon is produced to a lesser extent in the presence of hydrogen [5] is probably associated with the depression of CH₄ dissociation.

In conclusion, the production of SiC ultra-fine powder from silicon bulk in an arc plasma of a CH₄-based atmosphere, proceeds mostly via the sublimation of SiC which is produced in the bulk silicon. In order to verify this mechanism further, work on the direct arc plasma irradiation of a SiC bulk in various atmospheres is in progress.

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*Received 21 September 1988
and accepted 23 January 1989*