JOURNAL OF MATERIALS SCIENCE 25 (1990) 3101–3104

Production of ultra fine SiC powder from SiC bulk by arc-plasma irradiation under different atmospheres and its application to photocatalysts

YASUFUMI NARIKI, YASUNOBU INOUE*, KOHICHI TANAKA
*Department of Mechanical Engineering, and *Analysis Centre,*
Nagaoka University of Technology, Nagaoka, Niigata 940-21, Japan

The production of ultrafine SiC powder from a SiC bulk (containing 10 wt% Si) was examined by the arc-plasma method under different atmospheres such as argon, argon and hydrogen, argon and helium, and argon and nitrogen. No melting of SiC bulk occurred during arc-plasma irradiation, and even pure argon gas was effective for the production of the ultrafine powder. The SiC powder produced has the structure of β-SiC, compared to α-structure of the bulk SiC. The average particle size of the SiC powder produced decreased to one-half of the value when hydrogen or helium was added to argon. Smaller particles of SiC are formed by the arc-plasma gases with a large thermal conductivity. The present results confirm that sublimation is a major process in the production of ultrafine SiC powder. The SiC powder is found to be effective as a photocatalyst for the decomposition of water.

1. Introduction

In our series of works, the arc-plasma method has been applied to the production of ultrafine ceramic powder [1–4], and it has recently been shown that the arc irradiation of a silicon bulk in NH_3 and CH_4 gases leads, respectively, to the effective production of small particles of Si_3N_4 and SiC [3]. In the process of Si_3N_4 powder formation, it was suggested that a gas-phase reaction between evaporated silicon atoms and the surrounding NH_3 gas is responsible for the production; this process is plausible for the production of a compound powder. On the other hand, for SiC powder, we have proposed a mechanism in which a silicon carbide phase is first formed in the molten silicon bulk, after which its sublimation occurs as a major process in the production of SiC powder [4]. This process is unique and quite different from that of Si_3N_4 production. In the present work, in order further to establish the mechanism of the production of SiC ultrafine powder, and also to reveal the effects of different atmospheres, an SiC bulk was used as starting material and was irradiated under various arc-plasma atmospheres.

Silicon carbide exhibits semiconducting properties. As an effective material for the conversion of solar light energy, silicon carbide has been employed as photocatalyst in the synthesis of CH_3OH from H_2O and CO_2 [5, 6]. Because of its large surface area and specific properties, ultrafine SiC powder seems a promising photocatalyst. In the present work, a preliminarily study was made of the photocatalytic activity of SiC powder for use in the decomposition of water.

2. Experimental procedure

The arc-plasma furnace used for the production of ultrafine SiC powder was the same as described elsewhere [1–4]. A preliminary experiment showed that no successive arc-current discharge occurred for a pure SiC(99.9%) bulk in any type of atmosphere. However, the addition of a small amount of silicon to SiC permits a discharge, and thus silicon carbide bulk (α-SiC) containing 10 wt% Si (Shinetsu Chemical Co. Ltd) was employed in a cylindrical form as a starting material. The amount of free carbon was less than 0.02 wt%. Arc-irradiation was performed either in pure argon or in argon-based mixtures with helium, hydrogen or nitrogen such as Ar/He(50 vol%), Ar/H_2(10 to 50 vol%) or Ar/N_2(50 vol%). The chamber of the apparatus was evacuated and then flushed with argon or the mixtures. The total pressure during arc-plasma irradiation was maintained at around 0.1 MPa.

The structure of the SiC powder produced, as well as the bulk sample after arc irradiation, was analysed using an X-ray diffractometer (Rigaku RAD III). The microstructure and particle sizes of the powder were monitored by electron microscopy (Jeol, JSX 200 V). The surface area of the powder was measured by the BET method using nitrogen as adsorbate.

The photocatalytic decomposition of water was carried out in a closed circulation system with a quartz reaction cell in which 10 mg SiC powder catalyst was placed. Distilled and degassed water was transferred to the cell, and SiC was illuminated by 400 W Xe light through a band-pass filter (wave-length = 260 to 410 nm). The gases evolved were analysed using

0022-2461/90 $03.00 + .12

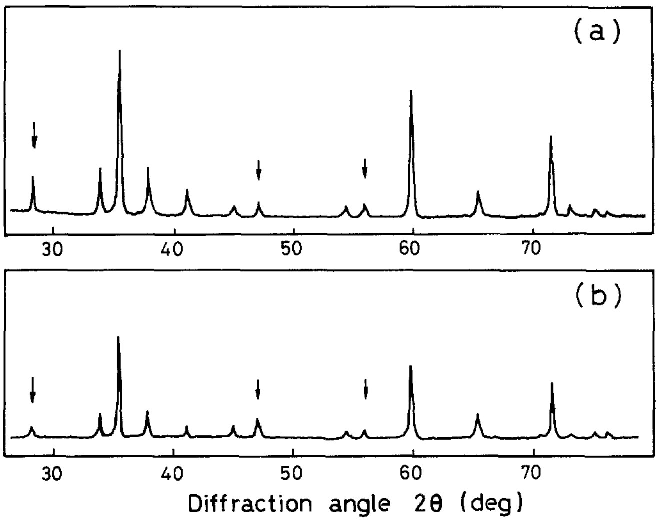

Figure 1 X-ray diffraction patterns of SiC bulk, (a) before arc-plasma irradiation, (b) after arc-plasma irradiation in argon atmosphere at 150 A for 60 sec. The arrows show silicon peaks.

a gas chromatograph connected to the reaction system. The amount of hydrogen evolved per unit time was taken as a measure of the photocatalytic activity.

3. Results

Both pure argon and its mixture with hydrogen, helium or nitrogen permits the production of ultrafine powder. The production of powder occurred without melting of the SiC bulk in which the original cylindrical shape was virtually retained during arc-plasma irradiation. The rate of powder production was 3 to 5×10^{-3} g sec^{-1} kW^{-1} when pure argon was used as plasma gas, and decreased to about a half that value when 50 vol % hydrogen was added to the argon gas.

Figure 1 shows X-ray diffraction patterns of SiC bulk before and and after arc-plasma irradiation. The starting material of SiC bulk has α-SiC structure in which the characteristic peaks are observed at $2\theta = 33.9°$ and 38.0°. The pattern involves small peaks due to silicon at 28.5°, 47.4° and 56.2°. After arc-plasma irradiation, the diffraction pattern of SiC remained almost unchanged. The ratio of diffraction peak intensity of silicon ($2\theta = 28.5°$) to SiC (35.8°) was 0.15 for the original SiC bulk and 0.10 after the arc-plasma irradiation. The arc-plasma irradiated SiC bulk lumps were cut into two pieces, and a section was examined by scanning electron microscopy. Neither voids nor new phases were observed, which was quite different from what was detected in the previous Si + CH_4 system [4]. Electron probe micro-analysis (EPMA) also showed that there were no appreciable inhomogeneous distributions of elemental carbon and silicon through the bulk. Figure 2 shows the diffraction pattern of ultrafine powder produced in an argon atmosphere. The general feature of the diffraction pattern is similar to that of SiC bulk, but there are marked decreases in peaks at $2\theta = 33.9°$ and 38.0°. This indicates that the SiC powder produced has a structure belonging to β-SiC. The ratio of diffraction peak intensity of silicon to SiC was 0.11. Figure 3 shows an infrared spectrum of SiC powder. A broad absorption peak at around 890 cm^{-1} is characteristic of the stretching vibration of the Si–C bond. There are negligibly small absorption peaks due to the stretching vibration of Si–O bonds (1100 cm^{-1}) as well as of O–H bonds.

In the electron micrographs of ultrafine powder, small round particles are observed, together with a small number of relatively larger hexagonal crystals. The morphology is similar to that of SiC obtained previously when a silicon bulk was irradiated in a CH_4 atmosphere [3, 4]. There are no significant differences between the shape of the fine powder produced by argon and argon plus hydrogen plasma gases. Figure 4 compares the size distributions of the SiC powder prepared in different arc-plasma atmospheres. The distribution profiles were determined by counting 2500 particles in the electron micrographs. It is shown that the profile gives the largest value at 12 nm for hydrogen and argon, 12 nm for helium and argon and 25 nm for argon, and the distribution profiles became narrower in the presence of either hydrogen or helium.

From the surface area measured by the BET method and assuming a round shape, the particle sizes were calculated to be 36 nm for the powder produced in hydrogen and argon, 52 nm for helium and argon and 97 nm for argon. These results reflect the differences in the particle-size distributions observed. Figure 5

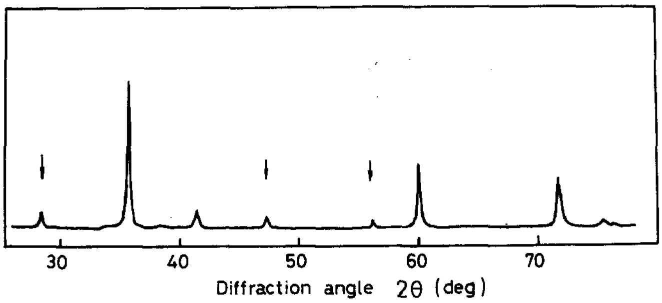

Figure 2 X-ray diffraction pattern of ultrafine powder produced in an argon atmosphere. Irradiation; 150 A for 60 sec. The arrows show silicon peaks.

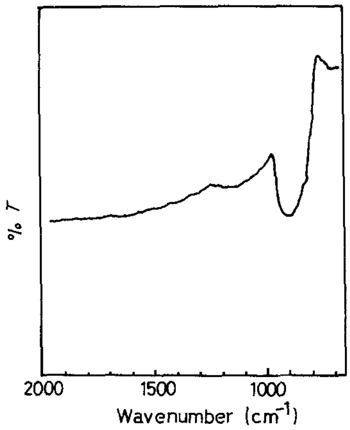

Figure 3 Infrared spectrum of ultrafine powder.

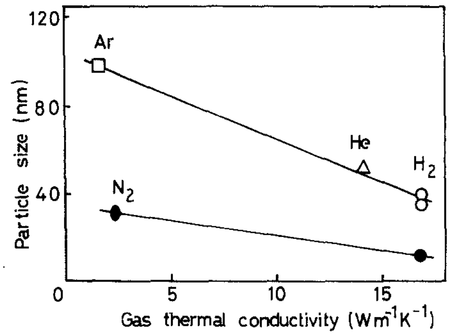

Figure 5 Relationships between average particle size of SiC produced and thermal conductivity of arc-plasma gas. Open symbols: SiC. Solid symbols: Si.

shows relationships between average particle sizes and thermal conductivity of arc-plasma gas. The figure also indicates the results on ultrafine silicon powder. it is interesting to see that the average particle sizes of both fine powders become larger with a decrease in the thermal conductivity of the surrounding gases.

In the photocatalytic activity of SiC powder during the decomposition of water, no evolution of hydrogen was detected without illumination. Figure 6 shows the evolution of hydrogen from water upon xenon lamp light irradiation. The evolution of hydrogen continued at a constant rate, but no oxygen was observed in the gas phase during the period of illumination. Although there is considerable dispersion in the photocatalytic activity of SiC powder obtained in the different arc-plasma gases, it remains in the same order of magnitude. The dependence of activity upon wavelength of light was preliminarily investigated, and it was shown that the activity began to be enhanced at around 400 nm and exhibited a drastic increase around 350 nm.

4. Discussion

One interesting feature in the present results is that the argon atmosphere is an effective plasma gas for the production of SiC powder from SiC bulk, although a small amount of silicon is required for the first arc-current discharge to occur. Another feature is that the presence of hydrogen in the arc-plasma gas tends to lower the rate of SiC production. This behaviour contrasts with the previous observation on the production of ultrafine silicon powder from a silicon bulk in which a pure argon atmosphere is ineffective, but hydrogen is an essential gas for the production. Such differences are indicative of their different production processes. As proposed previously [1], a plausible mechanism for the production of silicon powder is that melting of a silicon bulk and dissolution of hydrogen atoms are initial steps, followed by the evaporation of silicon atoms. The role of dissolved hydrogen is probably to liberate heat through its recombination and to accelerate the silicon evaporation. On the other hand, in the case of SiC powder formation, no significant melting of SiC bulk was observed while it was being arc-irradiated, thus indicating that the SiC bulk is able to gain enough heat merely from the argon arc plasma. These findings confirm a previously proposed mechanism that the sublimation of SiC is the main process in SiC powder formation.

The rate of SiC powder production observed in the present arc irradiation of the SiC bulk was larger by a factor of 30 to 50 than that estimated in the previous system where silicon bulk was irradiated in a CH_4 atmosphere [4]. It is reasonable to consider that the sublimation occurs more readily from solid SiC bulk, compared to a convecting SiC phase in the molten silicon in the Si + CH_4 system [4]. There were no significant differences in the ratio of X-ray diffraction peak intensity of silicon to SiC between the SiC powder and the arc-plasma-irradiated SiC bulk, thus indicating that neither decomposition of SiC nor segregational evaporation occurred.

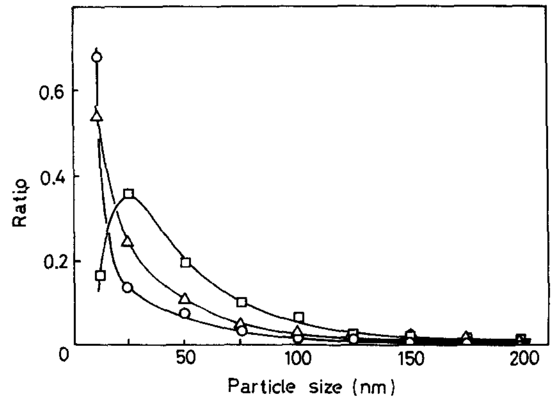

Figure 4 Particle distributions of SiC produced in different atmospheres. (○) Ar/H_2(50 vol %), (△) Ar/He (50 vol %), (□) Ar.

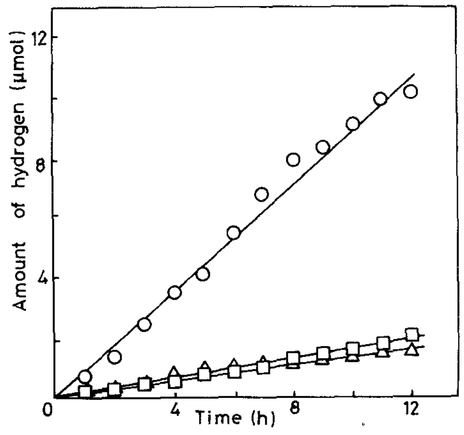

Figure 6 Hydrogen evolution from water on the ultrafine SiC powder surface under illumination. SiC produced in (○) Ar/H_2 (50 vol %), (□) Ar, and (△) Ar/He (50 vol %).

It is of interest to see that the SiC powder produced is in the β-SiC form, different from that of the starting SiC bulk. Because the bulk structure remained as α-SiC after arc-plasma irradiation, this indicates that not only particle growth but also structural transformation from α to β structure occurs simultaneously. Thus, it is reasonable to consider that the agglomeration of evaporated atoms or clusters proceeds in the gas phase in the vicinity of the surface while they are being subjected to cooling, through collisions with atmospheric gas molecules. The fact that the production of β-SiC is preferred at lower temperatures (1870 K) than that of α-SiC such as 4H, 6H and 15R (above 2100 K) [7–9] in basic polytypes is in line with this view. There is also a difference in the structures of SiC powder produced between the ($Si + CH_4$) system and the argon-irradiated SiC bulk system; the former favours the production of α-SiC as described [4], whereas the latter that of β-SiC. It is likely that this is due to the temperature difference upon sublimation, because in the former run the SiC phase is produced in the molten state of silicon and can obtain enough heat to form the structure of α-SiC powder from the surrounding silicon matrix.

As shown in Fig. 5, the particle size remains smaller in the atmospheric gases with larger thermal conductivity, which apparently indicates that faster cooling suppresses the growth of SiC particles. The smaller production rate of SiC powder in the presence of hydrogen might be related to the effects of decreasing the surface temperature of SiC bulk. If the dissolution of hydrogen atoms in the bulk SiC had occurred, the temperature of the bulk would increase by their recombination, as observed in the case of the silicon powder [1]. Because SiC bulk was maintained in a solid state during arc-irradiation, it is difficult for hydrogen atoms to be dissolved in the bulk. Furthermore, it seems likely that the sublimation takes place faster than the dissolution of hydrogen atoms.

In the photocatalytic decomposition of water, the evolution of hydrogen proceeds over a long period of illumination. No significant deterioration in the activity was observed in the range of experiments. From the wavelength dependence of light, the activity was found to be enhanced at around 350 nm. This onset wavelength is considerably lower than that of 410 nm corresponding to the band gap, 3.0 eV, of bulk SiC. Because the band gap becomes larger as the particle sizes of the semiconductors become smaller [10], it is likely that this activity enhancement is due to the absorption of light inherent in the band gap of SiC particles. No appreciable amount of oxygen was detected in the gas phase during the period of the experiments. The comparison of infrared spectra before and after the catalytic reaction showed that the absorption peak attributable to the stretching vibration of Si–O considerably increased after the reaction. This implies that a part of the oxygen produced is bound to the surface lattice of silicon atoms to form SiO. Furthermore, it is plausible that a part of the oxygen is converted to hydrogen peroxide in a similar way as observed in Pt/TiO_2 photocatalysts [11–13].

Because the percentage of surface area illuminated by light was not determined, the photocatalytic efficiency of SiC particles could not be accurately evaluated. Nevertheless, the activity per surface area is estimated to be almost the same order of magnitude as that of conventional photocatalysts such as Pt/TiO_2. In the present study, SiC powder was used without deposition of any metal or oxide as a catalytic promoting phase, and it is to be expected that the addition of such an active phase on the SiC surface might improve the photocatalytic capability.

References

1. K. TANAKA, K. ISHIZAKI, S. YUMOTO and T. EGASHIRA, *J. Mater. Sci.* **22** (1987) 2192.
2. K. ISHIZAKI, S. YUMOTO and K. TANAKA, *ibid.* **23** (1988) 1813.
3. K. ISHIZAKI, T. EGASHIRA, K. TANAKA and P. B. CELIS, *ibid.*, **24** (1989) 3553.
4. Y. INOUE, Y. NARIKI and K. TANAKA, *ibid.*, **24** (1989) 3819.
5. T. INOUE, A. FUJISHIMA, S. KONISHI and K. HONDA, *Nature* **277** (1979) 637.
6. B. AURIAN-BLAJENI, M. HALMANN and J. MANASSEN, *Solar Energy* **25** (1980) 165.
7. Y. INOMATA, M. MITOMO, Z. INOUE and K. TANAKA, *J. Ceram. Soc. Jpn.* **77** (1969) 130.
8. Y. INOMATA, Z. INOUE and K. KIJIMA, *ibid.* **77** (1969) 313.
9. Z. INOUE, S. SUENO, T. TAKAGI and Y. INOMATA, *J. Crystal Growth* **8** (1971) 179.
10. L. BRUS, *J. Phys. Chem.* **90** (1986) 2555.
11. H. MURAKI, T. SAJI, M. FUJITA and S. AOYAGUI, *J. Electroanal. Chem.* **169** (1984) 319.
12. D. DUONGHONG and M. GRATZEL, *J. Chem. Soc. Chem. Commun.* (1984) 1579.
13. J. KIWI and M. GRATZEL, *J. Phys. Chem.* **88** (1984) 1302.

Received 10 March
and accepted 17 August 1989