Silicon carbide micro-crystals grown from aqueous solution

It has been reported that the identification of polar surfaces of SiC is possible by etching with an alkaline solution containing $K_3Fe(CN)_6$. [1, 2] Harris *et al.* [1] reported that the etch pattern was selectively found on the silicon surface, but Kijima and Komatsu [2] observed similar patterns on the carbon surface and also found that the pattern was formed by a certain kind of deposit.

In the present work, structural and compositional identification of the deposit was performed by optical and scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and reflection electron diffraction. From the results of the experiments, it was concluded that the deposit mainly consisted of silicon carbide microcrystals. The formation of silicon carbide single crystal from alkaline solution without CN^- radical or ion has already been reported by Fujii [3] and co-workers.

Highly pure α-SiC single crystals (impurity concentration of the order of 10^{17} atoms cm^{-3}) prepared by a sublimation method [4, 5] were used as the substrate for the deposit. The crystals were cleaned by ultrasonic washing in acetone and placed in a Pyrex glass beaker containing an alkaline solution of $K_3Fe(CN)_6$(12.0 g $K_3Fe(CN)_6$ + 27.3 g NaOH + 50 g H_2O). After boiling the solution gently for about 30 min on a hot-plate, it was cooled to room temperature. A concentrated glutinous solution was removed by washing with distilled water or dilute HCl acid. The recovered substrates were dryed and used in the following observation. The details of the procedure are similar to those reported by Harris *et al.* [1].

The deposit had a yellowish tint. A typical deposit pattern is shown in Fig. 1. Such a pattern was only observed on the carbon surface [2] in the present work. The photographs in Fig. 2 show the pattern at different magnifications with SEM. Detailed observation showed that the deposit consisted of microcrystals having a size ranging from 100 to 1000 Å.

Fig. 3 is a fracture surface nearly parallel to the *c*-axis of the substrate. The deposit layer is distinguishable in the left hand part of the surface. Results of EPMA on the deposit layer show no marked difference compared with the substrate.

Fig. 4 is a reflection electron diffraction pattern from the deposit. Although the intensity of diffraction is very weak, all the diffraction rings were explained as being due to β-or α-SiC (especially 6H and 4H) polycrystals. In the photograph, the bright spots correspond to diffraction from the 6H substrate.

From the results stated above, the deposit is considered to mainly consist of SiC microcrystals. No marked change in the pattern shown in Figs 1 or 2 was observed after washing the deposit with concentrated HF + HNO_3 mixed acid, as reported by Kijima and Komatsu [2]. This also seems to support the conclusion.

Fig. 5 is a SEM photograph of a different part of the specimen shown in Figs 2 and 3. The upper, right, bright surface in the photograph corresponds to the silicon surface. In contrast with the work by Kijima and Komatsu [2], a surface skin or very thin surface layer seems to have developed on the initial silicon surface. Although, it has been reported that the polarity of the surface showing the pattern as in Fig. 1, was different between the

Figure 1 An optical micrograph of the deposit developed on a carbon surface of platy SiC single crystal.

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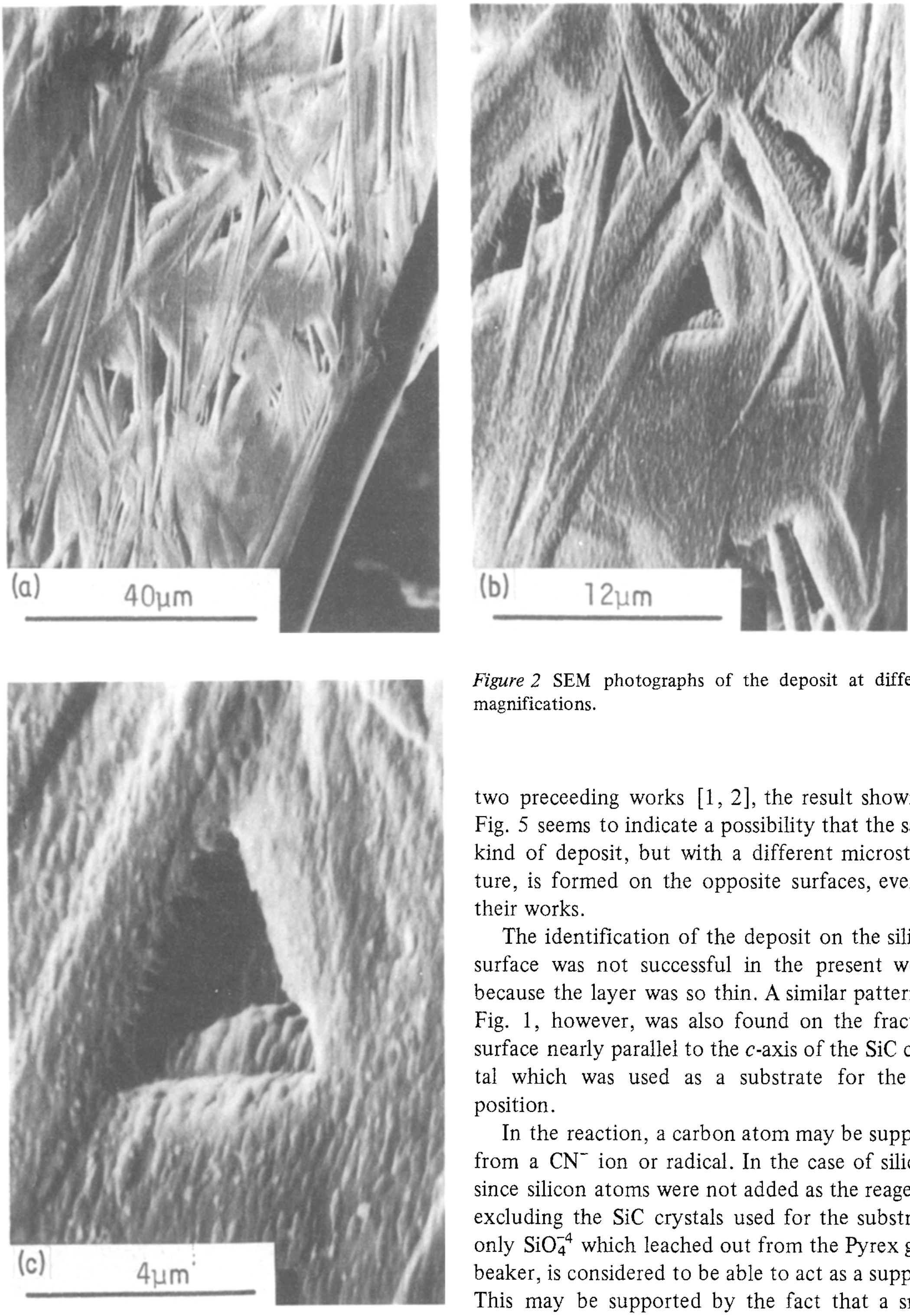

Figure 2 SEM photographs of the deposit at different magnifications.

two preceeding works [1, 2], the result shown in Fig. 5 seems to indicate a possibility that the same kind of deposit, but with a different microstructure, is formed on the opposite surfaces, even in their works.

The identification of the deposit on the silicon surface was not successful in the present work, because the layer was so thin. A similar pattern to Fig. 1, however, was also found on the fracture surface nearly parallel to the *c*-axis of the SiC crystal which was used as a substrate for the deposition.

In the reaction, a carbon atom may be supplied from a CN^- ion or radical. In the case of silicon, since silicon atoms were not added as the reagents, excluding the SiC crystals used for the substrate, only SiO_4^{-4} which leached out from the Pyrex glass beaker, is considered to be able to act as a supplier. This may be supported by the fact that a small

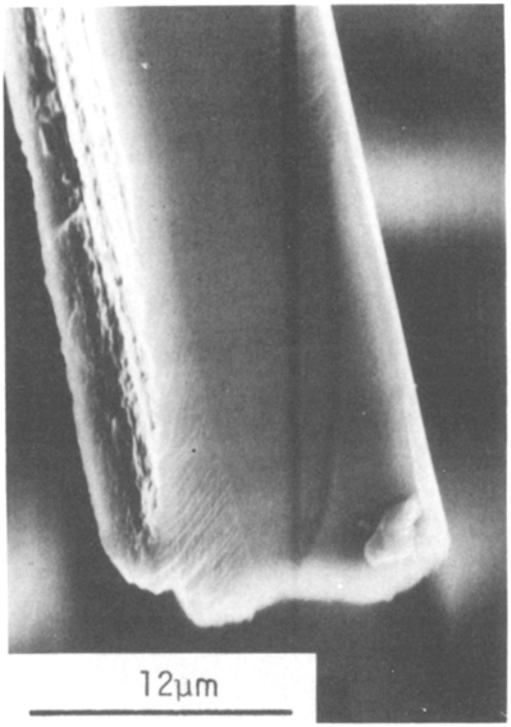

Figure 3 A SEM photograph of a fracture surface nearly parallel to the *c*-axis of the substrate. The specimen is the same one shown in Fig. 2. The layer of deposit is distinguishable in the left hand part of the fracture surface.

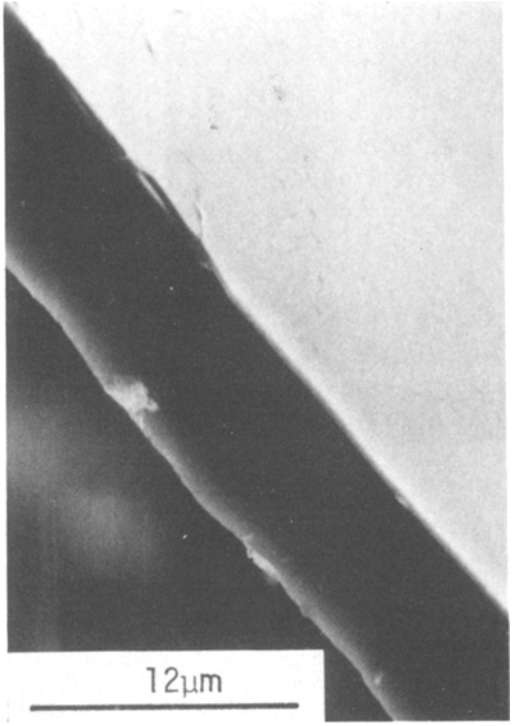

Figure 5 A SEM photograph of a fracture surface nearly parallel to the *c*-axis of the substrate. The photograph shows a different part of the specimen shown in Fig. 3. The bright surface in the upper right hand area corresponds to the silicon surface. The faint contrast and the morphology of the fracture surface seems to show the existence of a thin skin on the initial silicon surface of the substrate.

amount of colourless gel remained in the beaker after leaching the concentrated alkaline solution with dilute HCl acid.

The reduction of CN^- and SiO_4^{-4} is supposed to be realized by the oxidation of CN^- ions or radicals, but the actual process of the reaction is not clear.

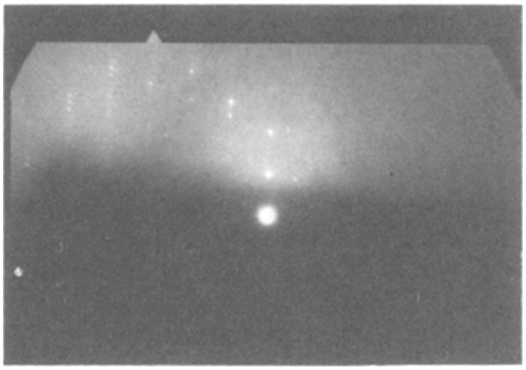

Figure 4 A reflection electron diffraction pattern from the deposit. The incident beam being nearly perpendicular to the *c*-axis of the 6H substrate. Clear and bright spots correspond to the diffraction from the substrate.

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The oxidation in air of sialon materials formed without densification aids

The importance of mobile cations at grain boundaries for the oxidation process in nitride ceramics has been convincingly demonstrated for the cases of hot-pressed silicon nitride containing magnesium oxide [1] and a commercial sintered sialon material [2]. In ceramics of these types there appears to be an ample reservoir of grain-boundary phase able to release cations such as Mg^{2+} and Y^{3+} to the surface oxide film to modify the properties of this film and to provide a basis for parabolic kinetics in the rate controlling diffusion of these ions from the grain boundaries.

Simple parabolic kinetics are, however, not always observed in the oxidation of sialon materials. In the course of recent studies on materials densified without the use of liquid-generating additives we have observed rather variable, but approximately linear, kinetics for a range of sialons with differing z values and O/N balances. While the data of Singhal and Lange [3], obtained with materials probably containing a much higher proportion of second phase than that present in our materials, do indicate parabolic kinetics, close examination of the published data of Arias [4] and of Hasegawa and co-workers [5] on the other hand shows that in these cases also, the parabolic rate law is not followed over the entire time range of the studies, particularly at longer times. Similar conclusions have been drawn by Brossard and co-workers [6, 7], from the examination of β'-sialon powders prepared with 60:40 and 70:30 balances of Si_3N_4:Al_2O_3, where it was observed that diffusion controlled oxidation kinetics were established only with difficulty at temperatures above 1300° C due in this case to crystallization of the protective amorphous oxide film.

Some of our own data obtained for oxidation of $z = 0.75$ sialons in laboratory air over the temperature range 1350 to 1550° C are presented in Fig. 1, and also, for convenience, in log–log form, in Fig. 2. The discontinuity in the curve at 1350° C is not an unusual, and so far not entirely explained, feature of the lower temperature oxidations. The mean value of the gradients of these plots is in the region of 0.81, and the apparent enthalpy of activation calculated at a constant extent of reaction has the very high value of 570 kJ mol^{-1}. Because the lines shown in Fig. 2 are approximately parallel, the enthalpy of activation is essentially independent of the extent of reaction up to times of the order of 16 h. These materials had been prepared by reaction hot-pressing at 1690° C mixtures of silicon nitride, aluminium oxide and aluminium nitride powders,

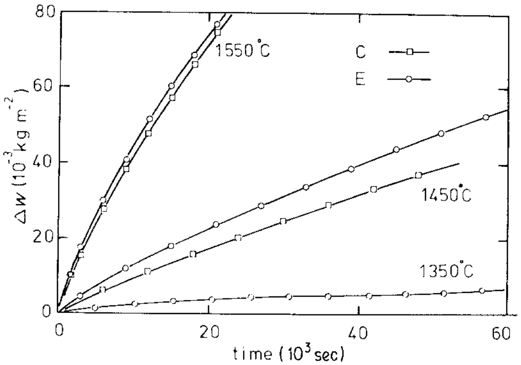

Figure 1 Weight gains (kg m^{-2}) plotted as a function of time (sec) for materials oxidized at 1350, 1450 and 1550° C.