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Microstructure of Si_3N_4–TiN composites prepared by chemical-vapour deposition

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The shapes and the distribution of TiN within Si_3N_4–TiN composites prepared by the chemical-vapour deposition of a $SiCl_4$–$TiCl_4$–NH_3–H_2 system have been examined using an electron microscope. The TiN dispersion in the amorphous Si_3N_4 matrix was granular and its maximum size was 3 nm. The TiN dispersions in α- and β-Si_3N_4 matrices were contained in their respective crystal grains; however, the shape of the TiN dispersions in the α-Si_3N_4 matrix was markedly different from that in the β-Si_3N_4 matrix. Granular TiN dispersions with an average size of 10 nm were observed in the α-Si_3N_4 matrix. On the other hand, the TiN dispersions in the β-Si_3N_4 matrix were columnar with a diameter of several nm having its axis extended to the direction parallel to the *c*-axis of the β-Si_3N_4 crystal.

1. Introduction

It is well known that various properties of ceramics are controlled not only by their chemical composition, but also by the sizes and shapes of grains and pores. Therefore, in evaluating a newly developed material, its microstructure must first be examined.

We have studied the synthesis of composites with Si_3N_4 matrices by chemical-vapour deposition (CVD) and obtained Si_3N_4–TiN composites from an $SiCl_4$–$TiCl_4$–NH_3–H_2 system [1, 2]. The details of preparation procedures for Si_3N_4–TiN composites and their crystal structure, preferred orientation, surface morphology and Ti content have been reported earlier [3]. The present paper presents the results of electron microscopic observation on the shape and distribution of TiN dispersed in the amorphous, α- and β-Si_3N_4 matrices.

2. Experimental procedure

Plate-like Si_3N_4–TiN composites were produced on a graphite substrate by CVD using a mixture of $SiCl_4$, $TiCl_4$, NH_3 and H_2 gases. The detailed preparation procedures have been reported [3]. Table I summarizes the preparation conditions and several properties of the samples which were subjects of the examination by electron microscopy in the present work.

The sample was removed from the graphite substrate and crushed into small fragments in an agate mortar. The fragments were dispersed in *n*-butanol and placed on the porous carbon supporting films, and then observed at magnifi-

TABLE 1 CVD conditions and some properties of samples

Deposition temperature, T_{dep} (° C)	Total gas pressure, P_{tot} (kPa)	Structure of Si_3N_4	TiN content (wt %)
1050	4	Amorphous	31.1
1250	4	α	4.5
1350	4	β	4.3
1350	8	β	3.6
1450	4	β	3.5

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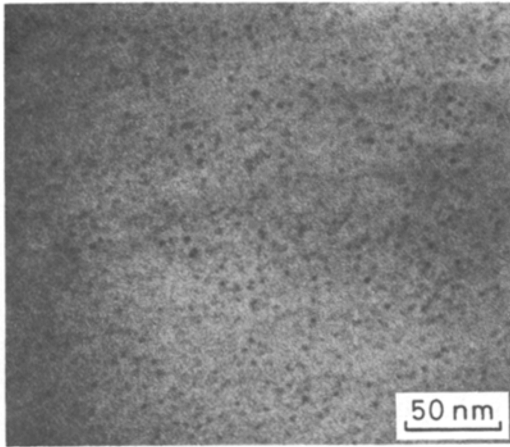

Figure 1 An electron micrograph of the deposit prepared at T_{dep} = 1050° C and P_{tot} = 4kPa.

cations of × 70 000 to 200 000 using a 1 MV electron microscope (JEOL, JEM-1000).

The X-ray microanalysis was also carried out using a microanalyser equipped with an energy dispersive X-ray detector (JEOL, EDS TEMSCAN-200CX). The diameter of the electron probe used was 30nm.

3. Results and discussion

Fig. 1 shows an electron micrograph of the deposit prepared at the deposition temperature (T_{dep}) of 1050° C and the total gas pressure (P_{tot}) of 4 kPa. Granular TiN dispersions are observed in the amorphous Si_3N_4 matrix and the maximum size of the dispersions is found to be 3 nm. As reported earlier [3], this sample gave very broad X-ray diffraction peaks of TiN and the size of the TiN crystallite was roughly estimated to be 3 nm from the half-value width of these peaks. The size of the TiN dispersions found in Fig. 1 is almost equal to the crystallite size given from the X-ray diffraction analysis.

Fig. 2 shows electron micrographs of the deposit, having an α-Si_3N_4 matrix, prepared at T_{dep} = 1250° C and P_{tot} = 4kPa. Figs. 2a and b were taken with the incident electron beam parallel and perpendicular, respectively, to the c-axis of the α-Si_3N_4 crystal. Since the TiN dispersions in the α-Si_3N_4 matrix are observed as Moiré or strain-contrast images, the crystal lattice of TiN dispersions has no definite orientation relation with that of the α-Si_3N_4 matrix. The size of the granular TiN dispersions in the α-Si_3N_4 matrix averages 10 nm which is larger than that in the amorphous Si_3N_4 matrix.

Fig. 3 shows electron micrographs of the deposit prepared at T_{dep} = 1350° C and P_{tot} = 4 kPa. The matrix here is β-Si_3N_4. Figs. 3a and b were taken with the incident electron beam parallel and perpendicular, respectively, to the c-axis of the β-Si_3N_4 crystal. Uniformly distributed TiN dispersions are clearly shown in Fig. 3a. It can be seen from Fig. 3b that these dispersions are columnar, with their axes extending parallel to the c-axis of the β-Si_3N_4 crystal. The diameter of the TiN columns is several nanometres. The observed image of the dispersions is very clear, because the crystal lattice of dispersions has a definite orientation relation with that of the β-Si_3N_4 matrix. The details of crystal lattice relationships will be reported in a forthcoming paper [4]. Figs. 4a and b show the energy-dispersive X-ray spectra for the

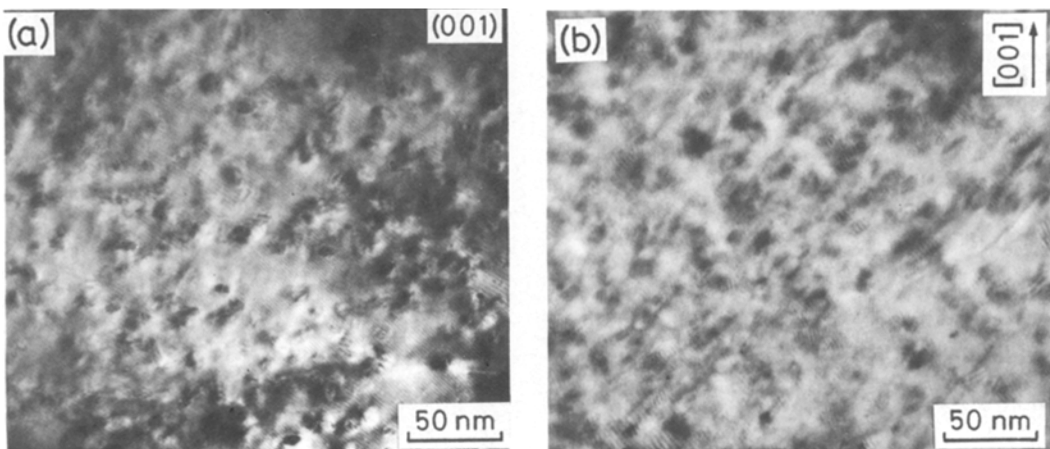

Figure 2 Electron micrograph of the deposit prepared at T_{dep} = 1250° C and P_{tot} = 4kPa.

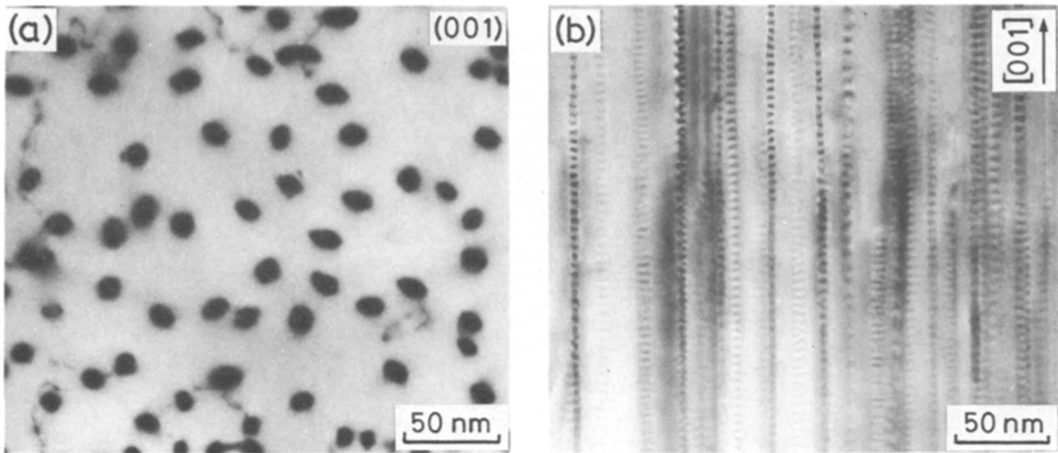

Figure 3 Electron micrographs of the deposit prepared at $T_{dep} = 1350°$ C and $P_{tot} = 4$kPa.

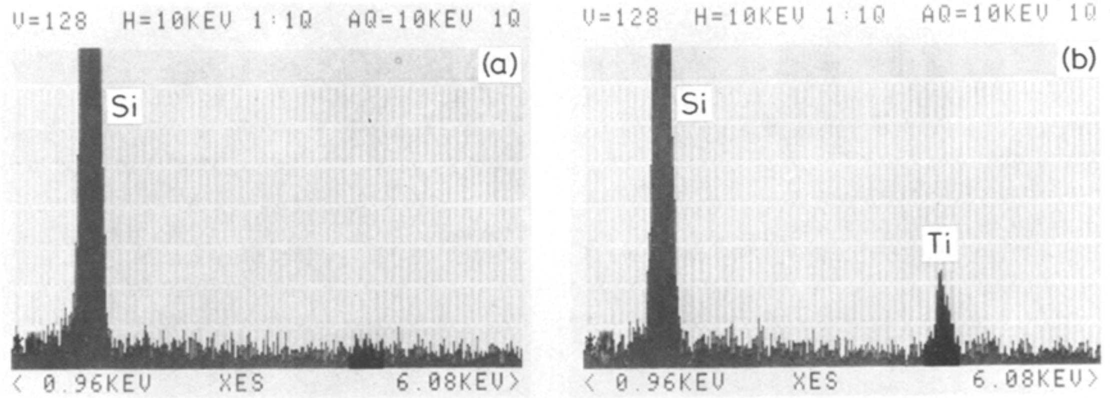

Figure 4 Energy dispersive X-ray spectra for β–Si_3N_4 matrix (a) and TiN dispersion (b).

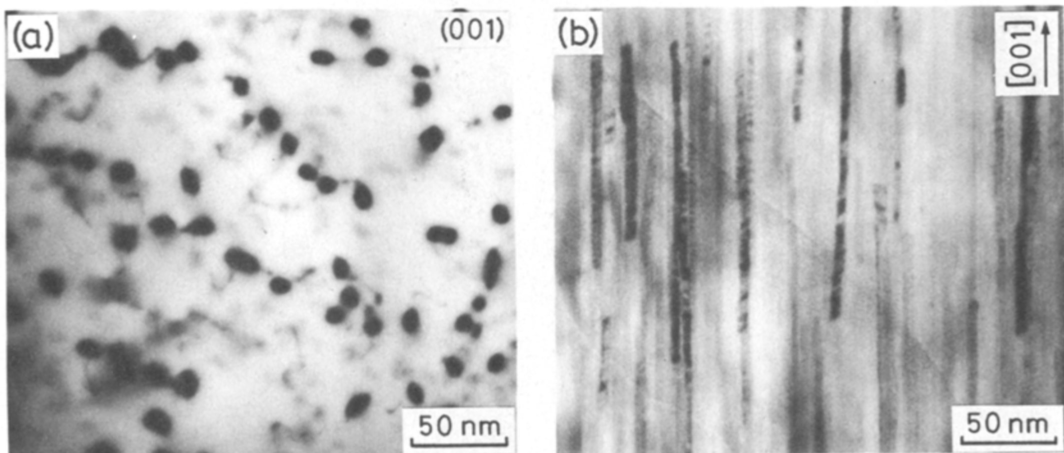

Figure 5 Electron micrographs of the deposit prepared at $T_{dep} = 1350°$ C and $P_{tot} = 8$ kPa.

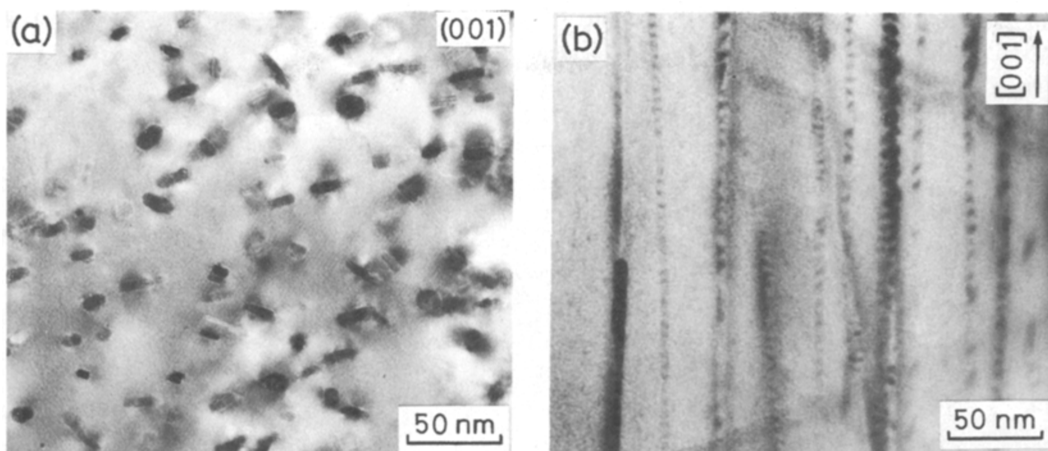

Figure 6 Electron micrographs of the deposit prepared at $T_{dep} = 1450°$ C and $P_{tot} = 4$ kPa.

Si_3N_4 matrix and for the TiN dispersion shown in Fig. 3, respectively. As seen in Figs. 4a only the spectrum of Si was detected from the matrix. This fact is in accordance with the previous results that the lattice parameters of the β-Si_3N_4 matrix in the Si_3N_4–TiN composites are very close to those of the pure β-Si_3N_4 and the solid solubility of Ti in β-Si_3N_4 is not significant [3]. Both Ti and Si peaks appeared in the spectra for TiN dispersions. The detection of Si is due to experimental conditions because the diameter of the electron probe is larger than that of the TiN columns.

Figs. 5 and 6 show electron micrographs of the Si_3N_4–TiN composites, having a β-Si_3N_4 matrix, prepared at different CVD conditions. The TiN columns in these β-Si_3N_4 matrices also had their axes extending parallel to the c-axis of the β-Si_3N_4 crystal. It can be seen from Figs. 3, 5 and 6 that the diameters of the TiN columns are practically independent of TiN content (cf. Table I).

Nickl and co-workers prepared several kinds of composites by CVD of $TiCl_4$–CCl_4–H_2 [5], $TiCl_4$–$SiCl_4$–CCl_4–H_2 [6], $SiCl_4$–CCl_4–H_2, $SiCl_4$–N_2–H_2, and $SiCl_4$–CCl_4–N_2–H_2 [7] systems and studied the microstructure of the composites by scanning electron microscopy. They reported that all deposits consisted of separate grains with two or three crystalline phases; however, the different phases intergrew coherently as lamellae of several microns thickness in the TiC–C, Ti_3SiC_2–TiC, Ti_3SiC_2–$TiSi_2$ and $Ti_5Si_3C_x$–TiSi deposits. Zirinsky and Irene [8] carried out an electron microscopic study of the Si_3N_4–AlN composites obtained by CVD of a SiH_4–$AlCl_3$– NH_3–H_2 system and found that AlN grains (smaller than several tens nm in size) were surrounded with amorphous Si_3N_4.

Fig. 7 shows schematic illustrations of the illustrations microstructure of TiN in the Si_3N_4–TiN composites prepared in the present study. Comparing our results with those of the related studies described above, the Si_3N_4–TiN composites have the following peculiar microstructures which

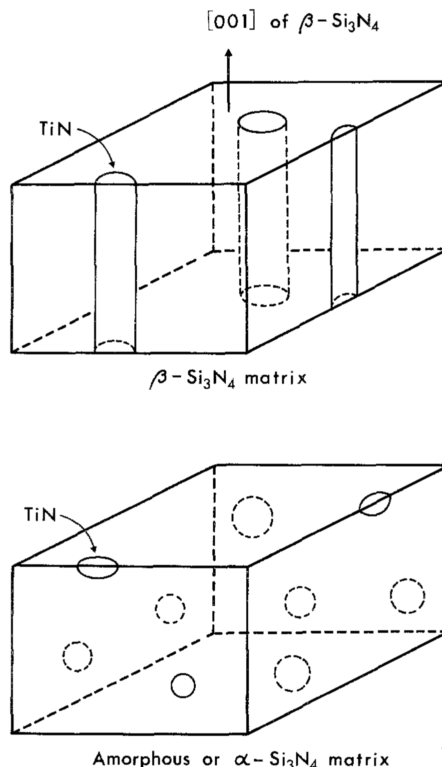

Figure 7 Schematic representations of the microstructure of the CVD Si_3N_4–TiN cmposites.

hitherto have not been observed in other CVD composites. 1. The TiN dispersions in the α- and β-Si_3N_4 matrices are contained in their crystal grains. 2. The TiN dispersions in the β-Si_3N_4 matrix are columnar. The cause of the difference found in the shape of the TiN dispersions between the α- and β-Si_3N_4 matrices is currently under investigation.

4. Conclusions

1. The TiN dispersions in the amorphous Si_3N_4 matrix were granular and the maximum size was 3 nm.

2. The TiN dispersions in the crystalline Si_3N_4 matrices were contained in the crystal grains.

3. The TiN dispersions in the α-Si_3N_4 matrix were granular and the average size was 10 nm.

4. The TiN dispersions in the β-Si_3N_4 matrix were columnar with a diameter of several nanometres. The columns extended their axes in the direction parallel to the *c*-axis of the β-Si_3N_4 crystal.

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