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The sinterability of ultrafine Si_3N_4

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Ultrafine amorphous Si_3N_4 with an average grain size of 30 nm was prepared by a thermal plasma method. The sinterability of the material depends strongly on the degree of crystallization and it is almost constant in a sample with a higher degree of crystallization than 40%. A problem with the sample when crystallized is that it is difficult to obtain a high green density compared with other samples prepared by conventional methods. However, if it was homogeneously mixed with sintering additives, it sintered to 98% density in an N_2 atmosphere. The microstructure of sintered bodies observed with an SEM and a TEM is briefly discussed.

1. Introduction

Si_3N_4 has high strength at high temperature, very good thermal shock resistance, and fairly good stability against oxidation. For these properties, it has been strongly considered as a material for a ceramic engine. However, it is difficult to sinter to a high density without additives, since it has very low diffusion coefficients of ions and a high vapour pressure. Therefore, many kinds of additives for sintering such as Al_2O_3, BeO, CeO_2, MgO, Y_2O_3 and so forth have been studied, as well as sintering at high N_2 pressure to avoid the decomposition of Si_3N_4, hot pressing, and hot isostatic pressing, to enhance the sinterability and phase relations.

Terwilliger and Lange [1] have studied the densification behaviour of Si_3N_4 with MgO during hot pressing. They concluded that MgO forms a liquid phase of a magnesium silicate and the transformation of α- to β-Si_3N_4 during hot pressing is not necessarily important for densification. Terwilliger and Lange [2] indicated from the sintering of Si_3N_4 with 5 wt % MgO at 1500 to 1700° C that a high density can be achieved when sintering is performed either for long periods at low temperature or short periods at high temperature. Loehman and Rowcliffe [3] have reported that the sintering of amorphous and crystalline Si_3N_4 with 4 to 17 wt % Y_2O_3 and 2 to 4 wt % Al_2O_3 at 1500 to 1700° C is by a liquid-phase mechanism, and several transient phases occur during sintering (depending on the starting composition) with sufficient heating. Mitomo [4] has successfully obtained high-density Si_3N_4 by the sintering in a high N_2 pressure, by which Si_3N_4 was protected from thermal decomposition at high temperature. Priest *et al.* [5] also sintered Si_3N_4 with CeO_2, MgO and Y_2O_3 to a high density at high N_2 pressure. Other studies of the sintering and phase relation of Si_3N_4 are extensive [6].

According to sintering theory, a smaller particle size without agglomerates is better for sintering densification. Rhodes [7] sintered partially stabilized zirconia to a high density at very low temperature by using ultrafine particles without agglomerates. Greskovich and Rosolowski [8] in the sintering of high-purity silicon suggested the importance of ultrafine powders for high densification. We have been trying to sinter ultrafine Si_3N_4 powder obtained from a thermal plasma method to a high density; however, it is difficult to sinter to a high density by using various additives. The main reasons for this are that the green density obtained by isostatic pressing at 2 ton cm^{-2} (199 MPa) is so low that a sintered body of high density is difficult to obtain, the homogeneous mixing of the Si_3N_4 with additives is not easy, and usually many cracks are generated in a sample during sintering under normal sintering conditions because of the very high shrinkage. In order to resolve these problems we made ultrafine Si_3N_4 into partially crystallized Si_3N_4 powder. In this paper we have studied the sinterability of the partially crystallized Si_3N_4 with Al_2O_3 and Y_2O_3, and the microstructure of the sintered bodies with scanning and transmission electron microscopes (SEM and TEM).

2. Experimental procedure

Ultrafine Si_3N_4 powder was obtained from thermal processing by using a combined-type reactor of arc- and high-frequency-induced thermal plasma, called a hybrid thermal plasma, as shown in Fig. 1. Plasma processing is very useful in preparing ultrafine powders for subsequent sintering. It is a vaporization–condensation process in which the cooling rate of particles in the plasma stream would be from 10^4 to 10^6 K sec^{-1}. A detailed description has been reported previously [9]. The ultrafine Si_3N_4 powder was amorphous and the average particle size 0.03 μm. It was heated at 500° C for 1 h in flowing N_2, in order to remove unreactive materials such as NH_3 and HCl. It was heat-treated again at 1300 to 1450° C for 1 to 4 h

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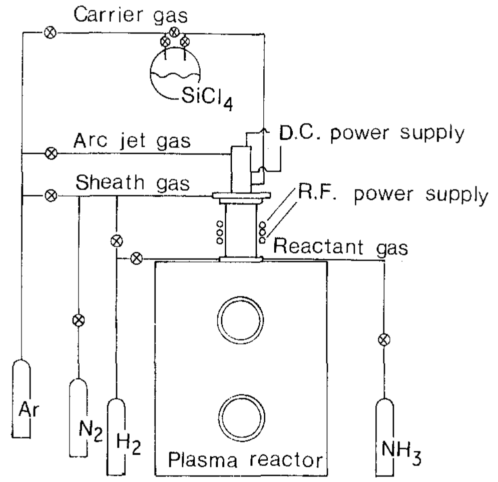

Figure 1 A schematic diagram of the thermal plasma apparatus by which ultrafine Si_3N_4 was prepared (⊗ = valve).

in an N_2 stream. The colour of the crystallized powder was slightly yellow and the average particle size about 0.2 μm. By this heat treatment, Si_3N_4 powders with various degrees of crystallization were obtained. The degree of crystallization of Si_3N_4 was determined by the X-ray powder diffraction method developed by Yamada *et al.* [10], as follows.

A total weight of 1 g sample with various ratios of perfect crystalline to amorphous Si_3N_4 was mixed with 0.1 g silicon. The plot of the degree of crystallization against the X-ray diffraction intensity of $(I_\alpha + I_\beta)/I_s$ gives a constant value of 0.093 as the slope, i.e.

$$\text{Degree of crystallization} = 0.093(I_\alpha + I_\beta)/I_s \qquad (1)$$

where I_α is the normalized average value of X-ray diffraction intensities such as (1 0 1), (1 1 0), (2 0 0), (2 0 1), (1 0 2), (2 1 0) and (3 0 1) in α-Si_3N_4; I_β; is the normalized average value of X-ray diffraction intensities such as (1 1 0), (2 0 0), (1 0 1) and (2 1 0) in β-Si_3N_4; and I_s is the normalized average value of X-ray diffraction integrated intensities such as (1 1 1) and (2 2 0) for silicon. The degree of crystallization in this experiment was determined by using Equation 1.

Futaki and co-workers [11] have studied the effect of Al_2O_3 and Y_2O_3 additives on the sintering of Si_3N_4. They have indicated that 4 wt % Al_2O_3 and 6 wt % Y_2O_3 are appropriate contents to sinter to a high density as well as high bending strength, so we used approximately the same values, 5 wt % Al_2O_3 and 5 wt % Y_2O_3, of the contents as additives.

The Si_3N_4 of various degrees of crystallization was mixed with 5 wt % Al_2O_3 and 5 wt % Y_2O_3 in an ethanol solution in an Si_3N_4 mortar for 30 min. After drying the powder, it was pressed at 250 kg cm^{-2} and then hydrostatically pressed at 2 ton cm^{-2} (199 MPa). The sintering temperature was from 1600 to 1800° C. A high-frequency-induced furnace was used for sintering as shown in Fig. 2. The samples were set in a carbon crucible with a powder bed of 50 wt % Si_3N_4 + 40 wt % h-BN + 10 wt % additives. These were then heated to a given temperature at a constant rate of 20° C min^{-1}. However, at this heating rate many cracks were generated in the sintered body of amorphous Si_3N_4, because of the very high shrinkage. Therefore, the amorphous sample was heated at a slow rate of 10° C min^{-1}. The colour of the sintered bodies was grey. The relative density was measured by the so-called Archimedes method. The green density of a compact was calculated from the value of the size and weight. One side of the sintered body was polished on a copper disc with diamonds to about 100 μm, then it was carefully polished to about 30 μm. Finally, the

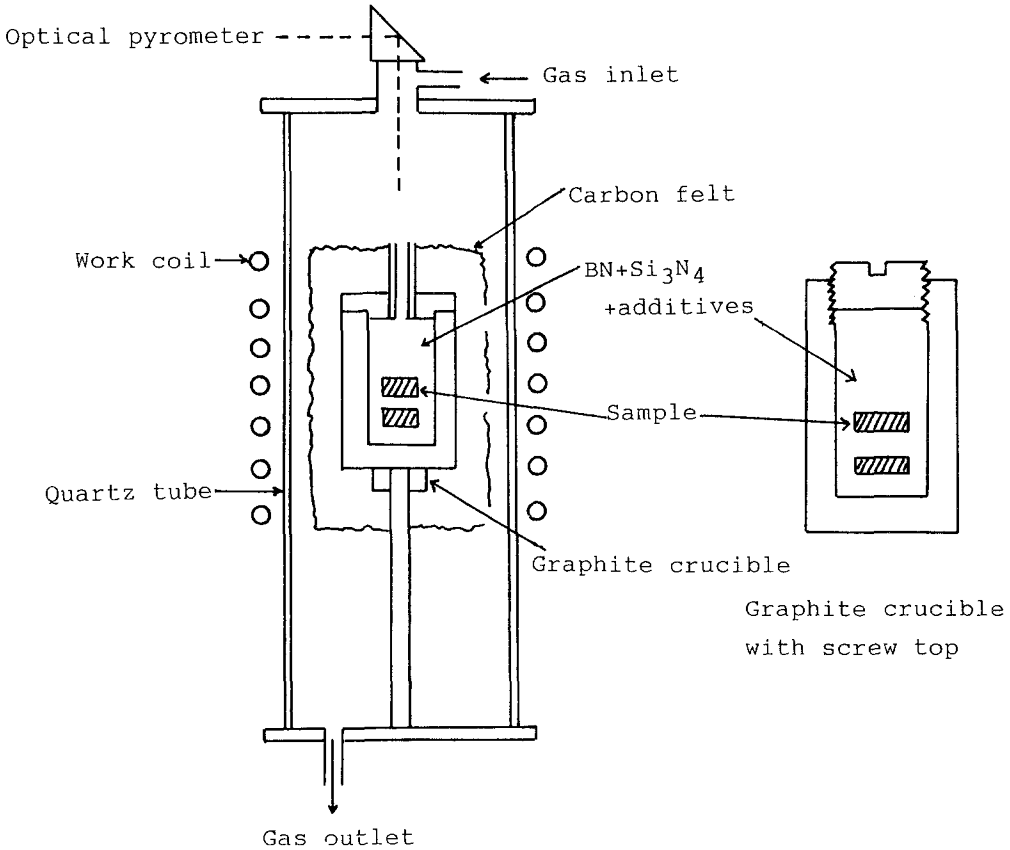

Figure 2 The sintering furnace used for Si_3N_4.

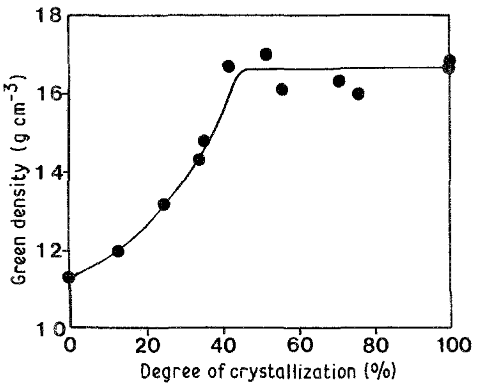

Figure 3 The relationship between green density and the degree of crystallization.

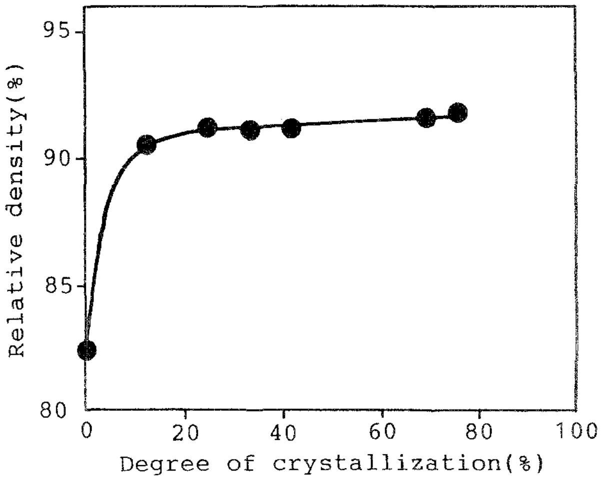

Figure 4 The relationship between relative density and the degree of crystallization.

resultant film was ion-thinned for observation with a TEM operating at 200 kV.

3. Result and discussion

It is well known that the value of the green density is very important for sinterability, therefore first of all we checked the relationship between the green density and the degree of crystallization (Fig. 3). The green density increases over the range of zero to 40% degree of crystallization. It is almost constant above 40% degree of crystallization.

The samples of various degrees of crystallization as shown in Fig. 3 were sintered at 1650° C for 1 h. The relative densities of the sintered bodies obtained are shown in Fig. 4. As can be seen in the figure, the density is strongly dependent on the degree of crystallization, particularly from zero to 10%. It is nearly constant for degrees of crystallization over 10%. Thereafter, we used Si_3N_4 samples with a high degree of crystallization of 70%. The different tendencies of the curves in Figs 3 and 4 are related to the homogeneous mixing of Si_3N_4 with additives, as discussed later.

It is of interest to compare the sinterability of Si_3N_4 obtained from plasma processing with those from other processes such as the decomposition of silicon imido, vapour deposition, nitridization of SiO_2 and direct nitridization of silicon. These physical properties are listed in Table I.

Si_3N_4 was mixed with 5 wt % Al_2O_3 and 5 wt % Y_2O_3 in an Si_3N_4 mortar with ethanol solution for 30 min. It was hydrostatically pressed at 2 ton cm^{-2} (199 MPa) and sintered at 1550 to 1800° C for 1 h in flowing N_2 with the high-frequency-induced furnace mentioned before. The sample obtained from the plasma method was used to compare with those of other methods.

The sintering data obtained are displayed in Fig. 5, where D = direct nitridization of silicon (Shinetsu Chemical Co. Ltd), D′ = direct nitridization of silicon (H. C. Starck), I = decomposition of silicon imido (Ube Industry Co. Ltd), R = nitridization of SiO_2 (Toshiba Ceramics Co. Ltd), C = vapour deposition (G. T. E., Sylbania) and P = thermal plasma (this work). As can be seen in the figure, every sample has a maximum density at 1700° C. The increase of relative density between 1550 and 1700° C indicates the effect of ion diffusion through the liquid phase on densification; on the other hand, the decrease of relative density above 1700° C shows that there was evaporation on dedensification.

In comparison with other samples, D and D′ have a different dependency of sintering shrinkage on temperature, that is, the relative density is almost constant, regardless of temperature. This is related to the high concentration of impurities such as iron, calcium and aluminium. For this, a liquid phase would be

TABLE I The preparation methods and impurities of various Si_3N_4 samples

Property	Maker and preparation method*						
	Toyosoda I	Ube I	G.T.E. C	Starck D	Shinetsu D	Toshiba R	This work P
Impurity							
N	38.0	37.9	37.3	37.6	37.2	37.1	
O	1.6	1.1	1.5	1.4	1.5	1.7	1.4
Cl	0.09	< 0.01					
Fe	0.0022	< 0.01		0.04	0.02	0.007	0.00n
Ca	< 0.001	< 0.005	< 0.0006	0.03	0.013	0.007	
Al	< 0.002	< 0.005	< 0.0002	0.06	0.15	0.002	0.00n
C	0.17		0.10	0.43	0.18	0.93	
Degree of crystallization (%)	100	100	60	100	100	100	70
α-Si_3N_4 (wt %)	89.4	96.9	> 95	94.5	> 92	93	> 95
Average particle size (μm)	< 0.6			0.5	0.52	1.0	0.2
Specific surface area (m^{2}g^{-1})	11.9	12	4	15	13.8		

*D = direct nitridization of silicon, I = decomposition of silicon imido, R = nitridization of SiO_2, C = vapour deposition, P = plasma method.

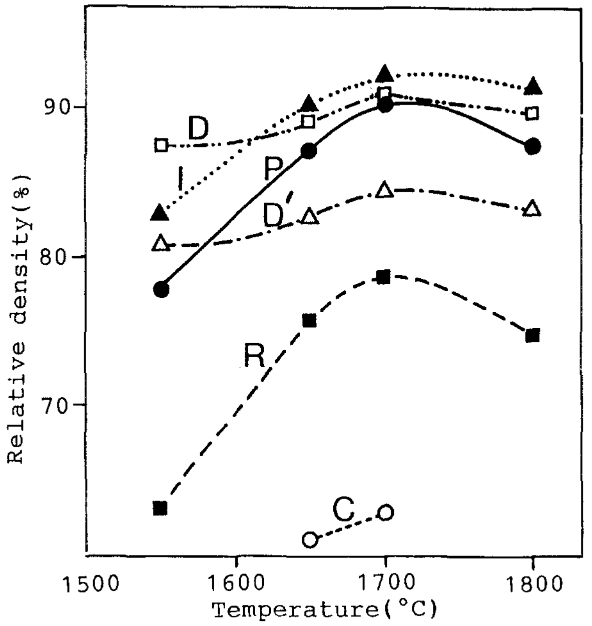

Figure 5 The relationship between relative density and temperature for various samples. D and D′ = direct nitridization of silicon, I = decomposition of silicon imido, R = nitridization of SiO_2, C = vapour deposition, P = thermal plasma (this work).

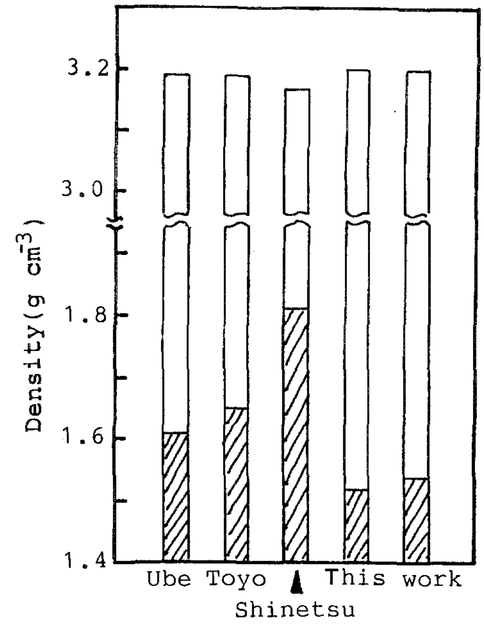

Figure 6 The relationship between sintered density and green density for various samples: Ube and Toyo (decomposition of silicon imido), Shinetsu (direct nitridization of silicon) and this work (thermal plasma).

formed at lower temperature. The difference of sinterability between D and D′ is due to that of particle size. The lowest relative density of C among various samples would be due to particles being needle-shaped, therefore the sinterability is no good because of the very low green density. The relatively low density of R would be related to its large grain size.

According to Fig. 5, Samples D and I have very good sinterability and the next best one is Sample P. The difference are very small. The discrepancy between them is considered to be due to inhomogeneous mixing of the samples with additives, since there is no difference in the following sintering data.

Samples D, I and P with 5 wt % Al_2O_3 and 5 wt % Y_2O_3 were ball-milled in a plastic crucible for 12 h by using Si_3N_4 balls in an alcohol solution. After it was dry, the material was isostatically pressed at 2 ton cm^{-2} (199 MPa), then the resultant sample was sintered at 1700° C for 1 h in a stream of N_2. As can be seen in Fig. 6, all the samples have approximately the same density. Therefore, the discrepancy among samples D, I, and P as shown in Fig. 5 is related to the inhomogeneous mixing of Si_3N_4 with additives, that is, homogeneous mixing offers a good sinterability of the sample, since sintering is a topochemical reaction.

Clearly, from Fig. 6, Sample P has the smallest green density; however, its final density is comparable to the other ones. The very large shrinkage indicates that Sample P is very easy to sinter. A problem with the sample is that there is microcrack generation in the sintered body. So if we have a Sample P with a high green density by a process such as high-pressure compaction, it would be very good to sinter to a high density.

Fig. 7 shows SEM micrographs of sintered bodies of samples D, I, and P. The microstructures are almost identical except for the small grain size of Sample I (Ube). The aspect ratio of the samples is about 4. Fig. 8 shows TEM micrographs of Sample P. As can be seen in the figure, all grains are wetted with a glassy

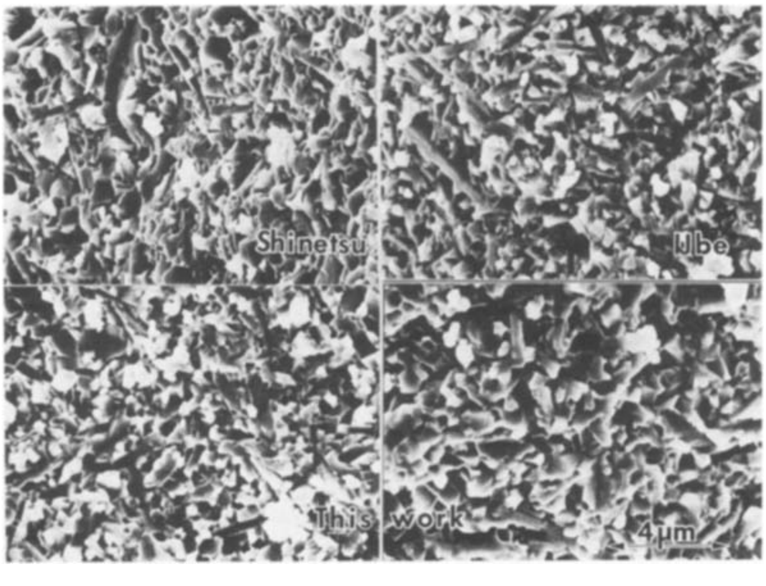

Figure 7 SEM micrographs of fracture surfaces in Si_3N_4 obtained from the decomposition of silicon imido (Shinetsu and Ube) and in this work.

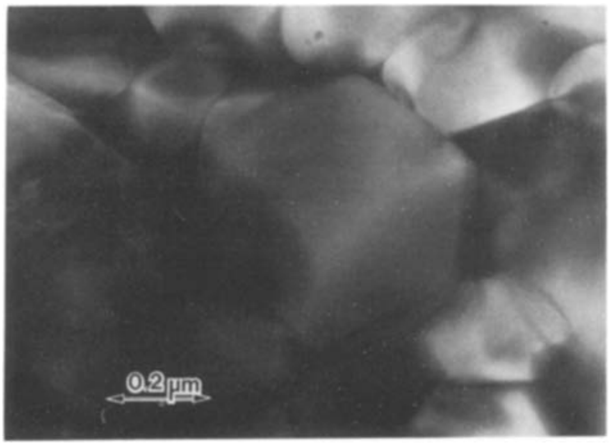

Figure 8 TEM micrograph of a sintered body of Si_3N_4 obtained from the thermal plasma method.

phase which has dark contrast. It seems that these have crystal habits. In fact, a micrograph viewed from the ⟨0001⟩ zone axis indicates a hexagonal plane (Fig. 9). This suggests that sintering grain growth takes place by diffusional transfer through a liquid. The curvature at the corner of the grain shown in Fig. 9 is due to surface tension. The slightly white contrast in the glassy phase around the grain would indicate phase separation by electron radiation.

In summary, ultrafine Si_3N_4 with an average grain size of 30 nm was prepared by a thermal plasma method. The green density and sintered density are much related to the degree of crystallization. The sinterability is almost constant in a sample with a higher degree of crystallization than 40%. It is difficult to obtain a high green density as easily as with conventional samples. However, if we mixed homogeneously the ultrafine Si_3N_4 with additives, it sintered to 98% density in an N_2 atmosphere. The microstructure observed with an SEM and TEM has been briefly discussed.

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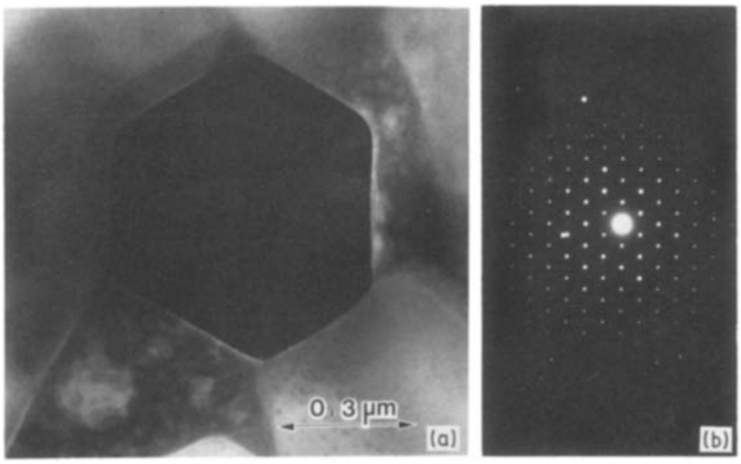

Figure 9 (a) A grain viewed from the ⟨0001⟩ direction; (b) ⟨0001⟩ diffraction pattern.