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Factors influencing the crystallization of ultrafine plasma-synthesized silicon nitride as a single powder and in composite SiC–Si_3N_4 powder

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A study of various parameters affecting the crystallization process of amorphous silicon nitride produced by plasma gas-phase reaction was undertaken to determine the conditions under which whiskers are formed. This process is influenced by the ammonium chloride content of the starting powder and the presence of nitrogen in the furnace atmosphere. This last parameter is also influential on the α/β phase ratio, along with other factors like the silica content, temperature and duration of the thermal treatment. Heat treatment at 1500 °C for 30 min under argon produced well-defined α-Si_3N_4 crystals with a hexagonal cross section, a mean length around 0.8 μm, and no sign of agglomeration. Under the same conditions, crystallization of silicon nitride in SiC–Si_3N_4 composite did not give crystals, but Si_3N_4 whiskers. Therefore silicon carbide plays a major role in their formation.

1. Introduction

Silicon nitride and SiC–Si_3N_4 composite powders have been produced from plasma gas-phase reaction in our laboratory [1, 2]. Because of the fine particle size, and the fluffy and amorphous character of the as-produced silicon nitride powder, it is not possible to obtain a green density sufficiently high for the sintering to proceed to full densification. It was thought that the solution could reside in the crystallization of the amorphous silicon nitride powder to induce the formation of α-phase Si_3N_4. But even crystallization according to published procedures [3–5] did not solve the problem, since this process induced the formation of fibres (whiskers) detrimental to the compaction of the powders. The aim of this study was to determine the influence of the following parameters on the crystallization: furnace atmosphere; maximum temperature; duration of treatment; and ammonium chloride and silica content of powders in order to identify the conditions under which Si_3N_4 whiskers are formed and therefore to suppress their occurrence.

2. Experimental procedures

The powders used in these experiments were synthesized following published procedures for SiC [6], Si_3N_4 [1] and SiC–Si_3N_4 composite [2]. The chemical compositions of the starting powders were as follows: SiC–Si_3N_4 composite made from the mixing of two synthesized powders of silicon carbide and silicon nitride (MIX); SiC: 42.4 wt %, Si_3N_4: 42.8 wt %, O: 4.4 wt %, NH_4Cl: 4.2 wt %, C (free): 2.5 wt %. SiC–Si_3N_4 composite made from the simultaneous plasma synthesis (SNC); SiC: 39.7 wt %, Si_3N_4: 44.9 wt %, O: 5.3 wt %, NH_4Cl: 2.3 wt %, C (free): 2.2 wt %. Silicon nitride (SN–A); N: 37.9 wt %, O: 3.8 wt %, NH_4Cl: 4.0 wt %. Infrared spectroscopy (IRS) was used to estimate the proportion of crystalline against amorphous phase and to evaluate the α/β ratio, as described by Luongo [7]. Infrared spectra were recorded on a Bomem Michelson 100 Fourier transform infrared spectrometer, with samples prepared as *K*Br discs. Chemical analyses C_{tot}, N_{tot} and O were performed on a LECO analyser. Free carbon analyses were run on a Coulometrics CO_2 coulometer, burning the samples at 720 °C for 20 min. Chlorine content was determined by ionic chromatography, for which samples were prepared as follows: 0.05 g of Si_3N_4 was dispersed in 5 ml of methanol in an ultrasonic bath, completed to 100 ml with water, and stirred. The resulting suspension was filtered with a 0.22 μm filter and injected by 50 μl portions in the column. The powders were observed by scanning electron microscopy (SEM) on a Jeol JSM 6100 instrument, to estimate qualitatively the proportion of whiskers, crystals and amorphous phase. Transmission electron microscopy (TEM) was used to identify the crystalline structure of the silicon nitride whiskers (Philips CM30, 300 kV). X-ray diffraction (XRD) patterns were recorded on a Philips PW 1840 diffractometer, using Cu radiation (wavelength, 15.425 nm). Thermal treatments were performed in a Marshall tubular furnace. The silica tube was purged before

TABLE I Heat treatment conditions for silicon nitride powders

Identification	Description	Heat treatment		
		Atmosphere	T_{max} (°C)	Time (min)
SN–A	As-produced powder			
SN–B	SN–A +	Air	500	5
SN–C	SN–A +	Air	700	30
SN–D	SN–A +	N_2	1500	30
SN–E	SN–A +	Ar	1500	30
SN–F	SN–B +	Ar	1450	30
SN–G	SN–B +	Ar	1475	45
SN–H	SN–B +	Ar	1500	1
SN–I	SN–B +	Ar	1500	10
SN–J	SN–B +	Ar	1500	30
SN–K	SN–B +	N_2	1500	30
SN–L	SN–B +	Ar	1500	120
SN–M	SN–C +	Ar	1500	30

heating, and the temperature at which the treatments were conducted (around 1500 °C) was reached in about 2 h.

3. Results and discussion

Table I presents the thermal treatments performed on the as-produced powders. They can be divided into two main categories: treatments on the as-produced powder (SN–B to SN–E); and heat treatments on pre-treated powders for the removal of ammonium chloride (SN–F to SN–M).

From the literature [3–5] it appears that the proper thermal treatment to induce the crystallization of amorphous silicon nitride is heating around 1500 °C in a nitrogen atmosphere. A sample (SN–D) was treated under these conditions for 30 min. Crystallization did occur, as demonstrated by infrared spectroscopy (Fig. 1). The resulting product, as shown in Fig. 2, includes an important amount of fibrous material along with well defined crystals and a small quantity of amorphous powder. TEM studies showed that the whiskers are α-Si_3N_4 with lattice parameters $a = 0.737$ and $c = 0.566$ nm. The presence of whiskers being detrimental to the compaction of the powder, a systematic study of several parameters was undertaken to eliminate their formation. One of these is the residual ammonium chloride content (around 4 wt %) of the as-produced powder, and two types of pre-treatment were applied to this powder in order to reduce its NH_4Cl content before subsequent crystallization treatment. The first pre-treatment exposed the powder to an air atmosphere at 500 °C for 5 min (SN–B). IRS revealed that the amount of ammonium chloride remaining after this treatment is less than 1 wt %, with negligible oxidation of the powder. The

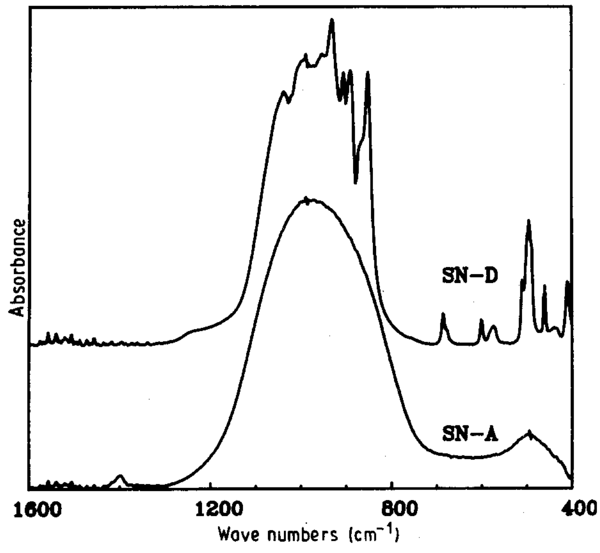

Figure 1 IRS of SN–A, as-produced amorphous powder; and SN–D, crystalline powder, α/β ratio: 78/22 wt %.

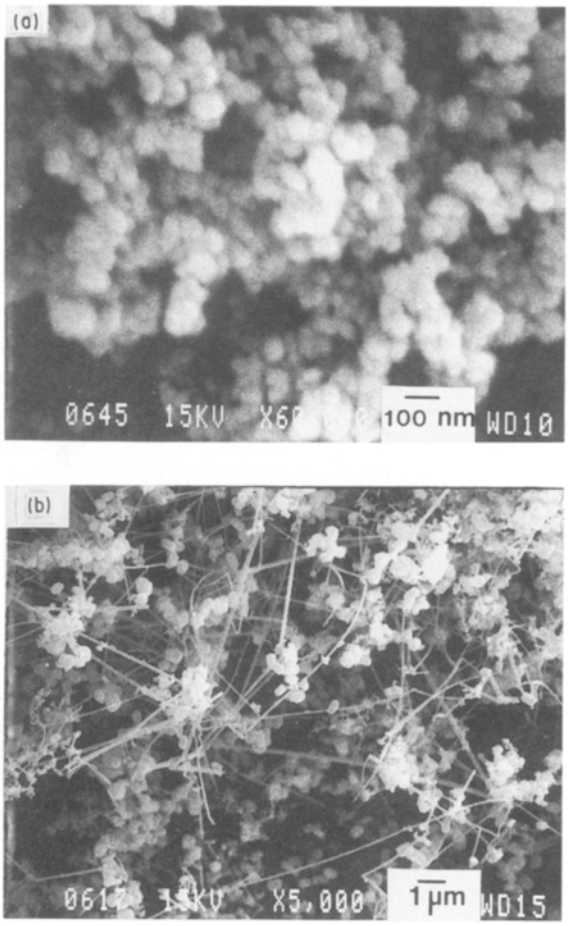

Figure 2 SEM photographs of (a) SN–A, as-produced powder; and (b) SN–D powder.

second pre-treatment involved the exposure of the as-produced powder to an air atmosphere at 700 °C for 30 min (SN–C). While no trace of ammonium chloride could be detected following this treatment, oxidation was more pronounced than in the first treatment.

3.1. Effect of furnace atmosphere

Following the first experiments, it was decided to crystallize the powder in an argon atmosphere instead of nitrogen, to determine if nitrogen was promoting whisker formation. Replacing the nitrogen atmosphere with argon, the as-produced powder was heat-treated at 1500 °C for 30 min (SN–E). The resulting powder was completely crystallized, and mainly composed of well-defined crystals having a hexagonal section and a mean length around 0.7 to 0.8 μm. However, there were still some isolated areas where whisker formation occurred. The proportion of whiskers in that sample was far less than observed under a nitrogen atmosphere. It seems that cutting this source of nitrogen is detrimental to the whisker formation. In Fig. 3, the infrared spectrum of SN–E shows that the crystallized powder is solely made of α-phase silicon nitride, compared to the 78/22 wt % α/β ratio evaluated for the SN–D powder, the main difference between the spectra of these samples being the presence of a band at around 578 cm^{-1}, characteristic of β-Si_3N_4 in SN–D. The intensity of that band, and of the one at 684 cm^{-1}, is used to evaluate the α/β ratio of the powder [7]. It appears that nitrogen in the furnace atmosphere plays an important role in whisker formation and is also influential in the formation of β-phase silicon nitride. Since cutting the source of available nitrogen in the system decreases the formation rate of whiskers, this was taken a step forward by the elimination of the other nitrogen source, ammonium chloride.

3.2. Effect of ammonium chloride content of the powder

Pre-treated powder for the removal of ammonium chloride (SN–B), with a NH_4Cl content less than 1 wt % (4 wt % in the as-produced powder), was heat-treated under argon at 1500 °C for 30 min (SN-J). From SEM observations (Fig. 4) it can be concluded that the presence of whiskers is almost eliminated and that the powder is constituted of well-defined crystal of α-phase silicon nitride. The crystals of α-Si_3N_4 are characterized by a hexagonal cross-section and a length between 0.7 and 0.9 μm, and do not seem to be agglomerated. From these results it is clear that ammonium chloride does have an effect in promoting the formation of whiskers, since heat treating under argon powders containing ammonium chloride produced a notable amount of whiskers (SN–E). It is however surprising that ammonium chloride is responsible for such an effect. On heating, ammonium chloride should sublimate or decompose to give nitrogen and chlorine derivatives at relatively low temperatures. We may believe that since the furnace is under a flow of argon, the gaseous species should be evacuated out of the furnace rather easily. Obviously this is not the case. Nitrogen derivatives (either N_2 or NH_3) coming from ammonium chloride decomposition play a role similar to nitrogen in promoting the formation of whiskers, except that ammonium chloride does not seem to induce the formation of the β-phase. To ascertain the influence of nitrogen gas, pre-treated powders for the removal of ammonium chloride (SN–B) were heat-treated under nitrogen at 1500 °C for 30 min (SN–K). That sample shows an important amount of whiskers along with crystals and some amorphous powder, demonstrating without a doubt the effect of nitrogen on whisker formation and also in promoting the formation of the β-phase, the α/β ratio being 82/18 wt %.

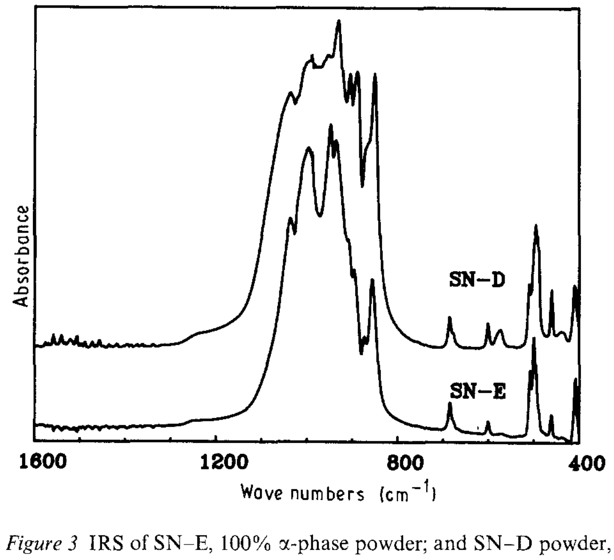

Figure 3 IRS of SN–E, 100% α-phase powder; and SN–D powder, α/β ratio: 78/22 wt %.

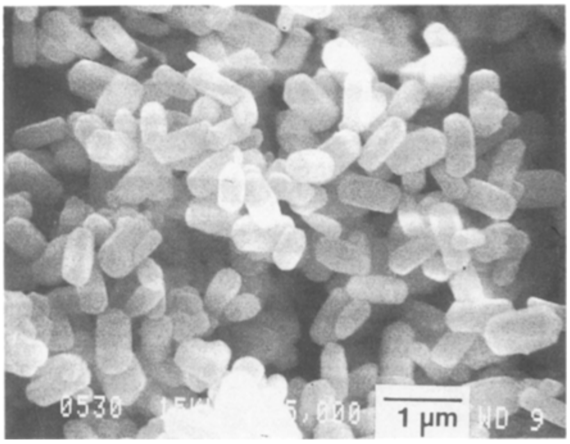

Figure 4 SEM photograph of SN–J powder.

3.3. Effect of temperature

From the preceding experiments we learned that to minimize the whisker content, ammonium chloride must be removed from the starting powder and argon used as the heat-treatment gas. We were now looking for the minimal temperature that could induce complete crystallization. Heat treatments were undertaken at 1450 and 1475 °C under argon for a 30 min period with the SN–B sample. The resulting powders were SN–F and SN–G, respectively. In both cases only

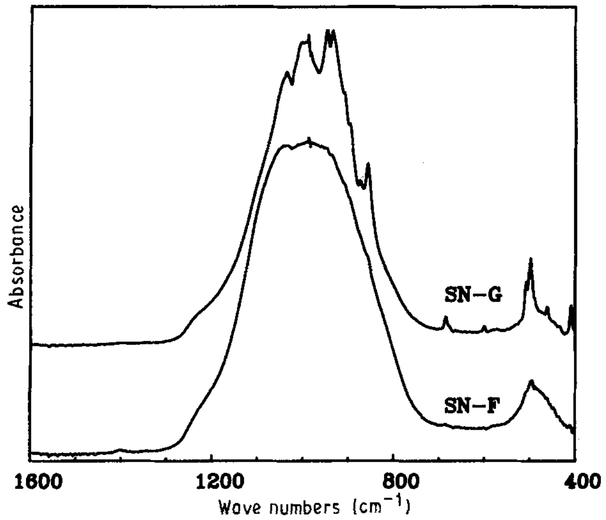

Figure 5 IRS of partly crystallized SN–F and SN–G powders.

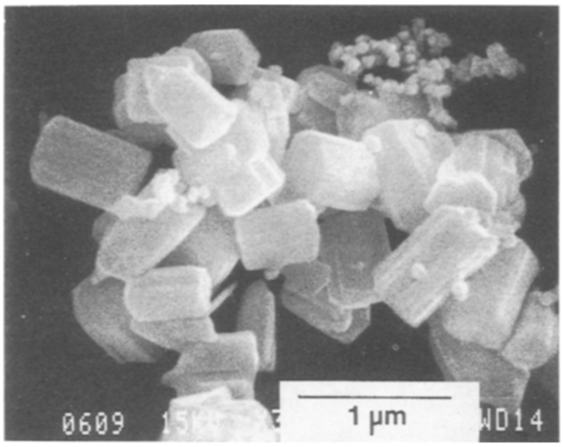

Figure 6 SEM photograph of SN–F powder.

partial crystallization took place (Fig. 5). In fact at 1450 °C, the proportion of crystalline material is very low, the powder being mainly amorphous as indicated by IRS and SEM photographs. The observed crystals had the characteristic shape described previously, with an average length between 0.5 and 0.7 μm for SN–F (Fig. 6) and between 0.6 and 0.8 μm for SN–G. The proportion of whiskers or fibres in the powder was very low. From these results we conclude that even if some crystallization took place at 1450 and 1475 °C, the minimal temperature for the complete crystallization of the amorphous powder must be very close to 1500 °C. Since some crystallization occurs below 1500 °C, it was thought that the duration of heat treatment at the maximum temperature could also be an influential factor.

3.4. Effect of time duration at maximum temperature

This study was performed with the SN–B powder, heat treated under an argon atmosphere for four time periods. The results for 30 min are already known: complete crystallization forming well-defined crystals of α-phase silicon nitride. Lowering the duration to 10 and 1 min affected the morphology of the resulting powder (SN–I and SN–H, respectively) in the following way: the crystallization was not completed, in fact most of the powder was still amorphous. This was particularly evident for the duration of 1 min, for which whiskers or fibres were not present or are very rare. The crystals observed in both cases seemed to be of the α-phase. It appears that the only effect of using a shorter time period is to lower the degree of crystallinity. However, extending the time at this temperature beyond 30 min (SN–L) induced major modifications to the aspect of the powder as presented in Fig. 7. The powder was completely crystallized, but long fibres were formed and from the SEM observations seemed to come from the partial sintering of individual particles or crystals. When fibres were not formed, individual crystals were not seen, but rather agglomerates of partly sintered crystals. The α/β ratio was evaluated at 78/22 wt %, and this was solely due to duration time, as all the other heat treatments described so far, using SN–B powder under argon atmosphere, produced only α-phase silicon nitride. From these results, it is clear that the duration time at the maximum temperature has an effect on the crystallization process. There is a minimum time for complete crystallization, and as the time period increases the formation of fibres coming from the partial sintering of individual crystals occurs. Longer duration also promotes the formation of β-phase silicon nitride.

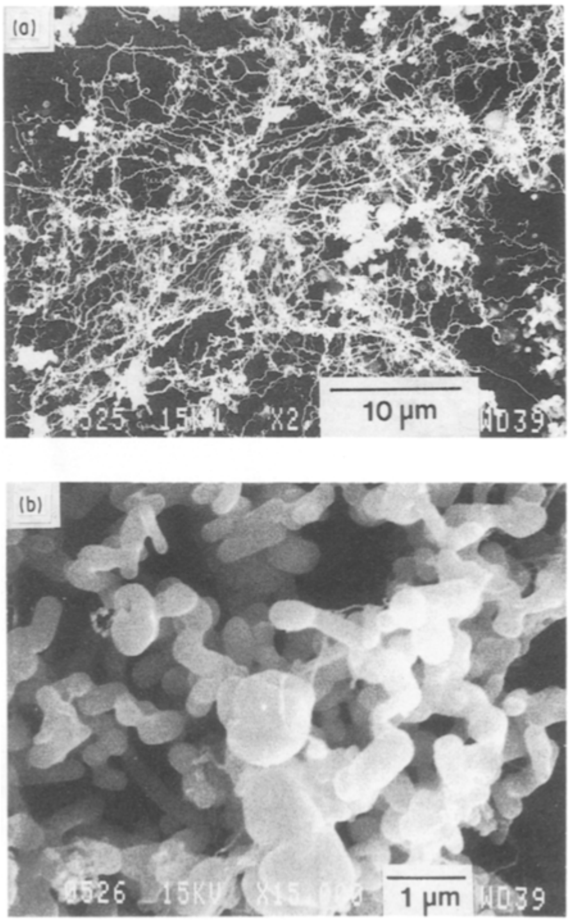

Figure 7 SEM photographs of SN–L powder: (a) overview of the long fibres formed; (b) sintering of individual crystals or particles.

3.5. Effect of silica content

A pre-oxidized powder (SN–C) was heat-treated at 1500 °C under argon for 30 min (SN–M). The resulting powder presented the following characteristics: partial crystallization, very low content of fibres or whiskers, and usually well defined crystals found along with amorphous powder. The α/β ratio was estimated at 75/25 wt %. In comparison with the results obtained for the SN–J powder, greater oxidation or a greater amount of silica in the powder seemed to decrease the degree of crystallinity, did not contribute to the formation of whiskers, but promoted the formation of β-phase silicon nitride.

3.6. Crystallization of Si_3N_4 in SiC–Si_3N_4 composites

As the crystallization of silicon nitride was characterized and the factors influencing the presence of whiskers were known (Table II), attempts to induce the formation of the α-phase silicon nitride in the as-produced Si_3N_4/β–SiC composite powders containing amorphous silicon nitride were undertaken. Two types of composites were simultaneously treated; powders produced in a one-step process (SNC); and the composite formed by mixing silicon nitride and silicon carbide powders produced individually by plasma gas-phase reaction (MIX). Table III shows the conditions in effect for the thermal treatments. The heat treatment situation is similar to that presented in the case of silicon nitride. The as-produced powders were heat-treated under argon at 1500 °C for 30 min (SNC–C and MIX–C), and the results are compared to those for the pre-treated powders for the removal of ammonium chloride (SNC–A and MIX–A) heat-treated under the same conditions (SNC–B and MIX–B).

TABLE II Summary of observed effects

Furnace atmosphere:	Nitrogen promotes the formation of whiskers as well as the formation of β-phase silicon nitride. Argon is not a factor in the formation of whiskers or β-phase.
Ammonium chloride:	The presence of ammonium chloride in the starting powder favours the formation of whiskers but does not influence the formation of the β-phase.
Silica:	Higher silica content slows the crystallization process. It does not promote whisker formation but favours the production of β-phase.
Temperature and time:	There is a minimal temperature that induces complete crystallization (around 1500 °C). Higher duration at this temperature promotes the formation of the β-phase, along with partial sintering of the crystals to form agglomerates and fibres. There is probably an inverse relationship between maximum temperature and duration. If the maximum temperature is raised, the duration should be decreased.

The results obtained show no difference between the composite powder produced in a one-step process and that produced from mixing the two constituent powders, except maybe a more uniform distribution in the powder produced in the one-step process. In addition, there was no difference between the pre-treated and as-produced powders in regard to the product obtained after the heat treatment at 1500 °C. There are no well-defined crystals of the size seen previously, only whiskers and starting powder (Fig. 8). This type of result gives some hints about the formation mechanism of the well-defined characteristic crystals found in silicon nitride. The crystals should be formed in the solid state, from joining of amorphous particles and reorganization. The absence of these crystals in the composite materials indicates that their formation is probably restricted by the fact that the joining of amorphous particles is hindered by silicon carbide particles incorporated in the process. Even though large crystals of silicon nitride do not form, crystallization of the amorphous phase takes place, as revealed by XRD patterns of the as-produced powder (Fig. 9a) and of the same powder after heat treatment (Fig. 9b). This shows that the only peaks detected for the as-produced powder are those related to β-SiC, while those related to α-Si_3N_4 are evident in the heat-treated powder, confirming the crystallization of amorphous silicon nitride. The composition of isolated whiskers was determined by energy dispersive X-ray (EDX) analysis. Only silicon nitride whiskers were found.

TABLE III Heat treatment conditions for composite powders

Identification	Description	Heat treatment		
		Atmosphere	T_{max} (°C)	Time (min)
SNC[a]	As-produced powder			
MIX[b]	As-produced powder			
SNC–A	SNC +	Air	500	5
MIX–A	MIX +	Air	500	5
SNC–B	SNC–A +	Ar	1500	30
MIX–B	MIX–A +	Ar	1500	30
SNC–C	SNC +	Ar	1500	30
MIX–C	MIX +	Ar	1500	30

[a] SNC = simultaneously synthesized Si_3N_4 and SiC.
[b] MIX = blend of individually synthesized Si_3N_4 and SiC.

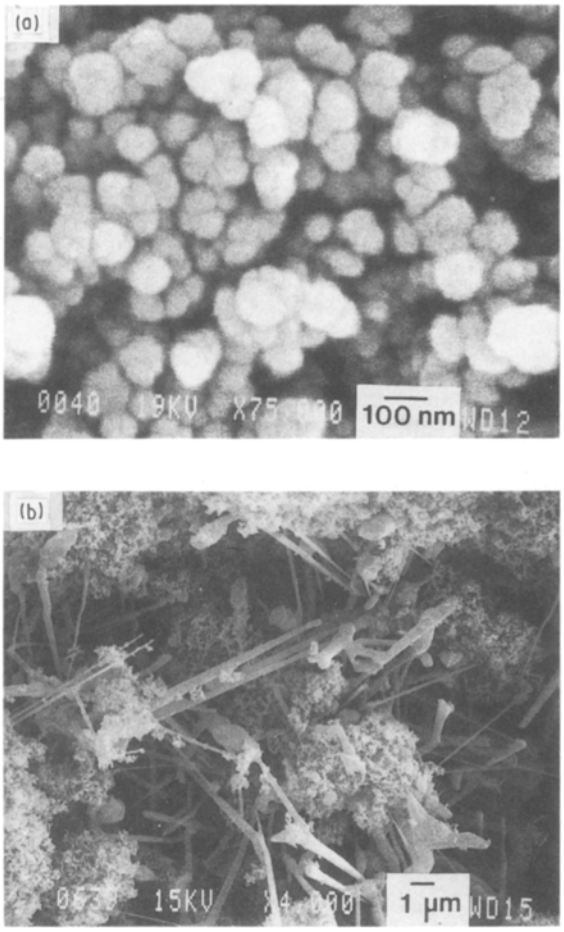

Figure 8 SEM photographs of (a) SNC, as-produced powder; and (b) SNC–B powder.

The presence of whiskers in that proportion is at first surprising, since no ammonium chloride or nitrogen is involved. Other factors must therefore be taken into account, such as the free carbon content and the presence of silicon carbide. Although no study on the formation mechanism of the Si_3N_4 whiskers was undertaken, the authors believe that they are the result of a series of single-step reactions involving SiC and Si_3N_4, and also intermediates like SiO_2, Si_2N_2O, SiO and C.

4. Conclusions

The main factors contributing to the formation of whiskers in the crystallization process of amorphous silicon nitride are the ammonium chloride content of the starting powder, and the presence of nitrogen in the furnace atmosphere. Crystallization under argon at 1500 °C for 30 min with powders pre-treated for the elimination of ammonium chloride gave the best results, forming well defined α-Si_3N_4 crystals with a hexagonal cross section, a mean length around 0.8 μm, no sign of agglomeration and no whiskers.The α/β ratio in the powder is controlled by parameters such as nitrogen in the furnace atmosphere, silica content, higher temperature and duration, all of these contributing to increase the β-phase content. The crystallization process of amorphous silicon nitride in SiC–Si_3N_4 composite does not follow the same path as even in conditions unfavourable for their appearance (argon atmosphere, 1500 °C, 30 min) silicon nitride whiskers are formed.

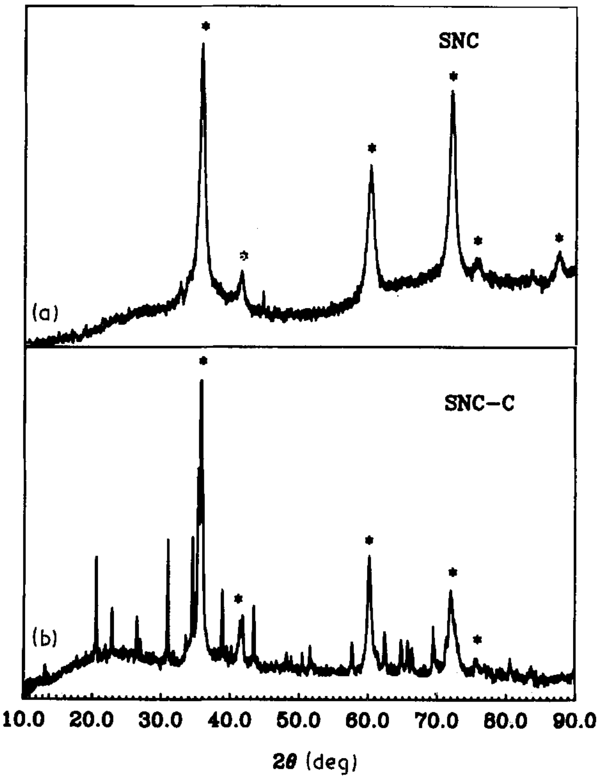

Figure 9 XRD patterns of (a) SNC powder, amorphous Si_3N_4/β–SiC; and (b) SNC–C powder, α-Si_3N_4/βSiC. *, peaks associated to β-SiC.

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