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Formation and Characterization of α-Si_3N_4 Whiskers from Laser Synthesized Nano Amorphous Si–N–C Powders

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Abstract: α-Si_3N_4 whiskers have been prepared from the laser-synthesized nanometric amorphous Si–N–C powders at 1873 K under 1 atm N_2. The as-formed whiskers were characterized by TEM, STEM, FTIR and XRD techniques and the process conditions were studied. The whiskers exhibit four types of morphologies: the long, thick, straight, the prismatic, the ribbon-like, and knuckled whiskers. The gas phase reaction among N_2, SiO, and CO gases leads to the formation of Si_3N_4, nucleated on the pre-crystallized α-Si_3N_4 grains, which ensures an *in situ* formation, and grows rapidly by a VS mechanism along specific crystal planes such as {1101}. Thermochemical analysis indicates that the higher Si_3N_4 whisker formation temperature of 1873 K for the gas phase reaction results from the lower P_{CO}/P_{SiO} ratio in the Si–N–C system.

1 INTRODUCTION

Si_3N_4 whiskers have many superior mechanical properties, such as toughness and good high-temperature strength, and have important structural applications as reinforcing materials. Although the sintering study on the whiskers as reinforcing materials is less than the extensively studied SiC whiskers, it has been used to reinforce light metal,[1–3] ceramic,[4] and plastic.[5] The superplastic Si_3N_4(w)–Al can be achieved[1] by whisker reinforcement and the composite exhibits a high tensile strength and good machinability—even higher and better than those of the SiC(w)–Al composite.[3] Additionally, the Si_3N_4 reinforced Al_2O_3 has strength and toughness about 20% and 50% higher than those of the monolithic matrix materials.[4]

Generally, the Si_3N_4 whiskers can be synthesized from Si (solid or liquid) + N_2(g),[6,7] silica (or silica-containing compounds) + C[8–12] and $SiCl_4$ (g) (or silicon halide) + N_2 + NH_3 (+Fe or Co catalysis) system,[13,14] and the Si_3N_4 whiskers with various morphologies such as α–Si_3N_4, β–Si_3N_4,[15] amorphous Si_3N_4,[16] and β-sialon[12] can be obtained. In these methods, only the silica carbonthermal reduction has been used in industrial production of the Si_3N_4 whiskers[5] because of the lower raw material cost compared with the others such as the high purity Si powders used in silicon nitiriding. One shortcoming of this method is the presence of unreacted C or SiO_2 in the whiskers which need to be removed from the whiskers by heat treatment.[12] However, the impurity coming from the spherical droplets on the whisker tips due to the VS whisker formation mechanism is rarely removed, but greatly influences the mechanical properties of the as-sintered bodies.[17,18] Also, whisker nucleation baffle in the silicon nitridation method[7] and the required addition of Fe or Co catalyst[13,14] in the silicon halide method also introduced various impurities in the whiskers besides the lower whisker yielding rate and the higher cost of the raw materials in these methods.

The present paper reports on the formation of high purity α-Si_3N_4 whiskers from the low cost

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nano-amorphous Si–N–C powders and characterization results of the whiskers. Due to the combination of the elements on atomic scale, no premixing process is needed, quite different from that in the SiO_2–C system, between which a uniform mixing is critical to reduce the impurity in the whiskers. As will be seen, the absence of any other catalyst or solid Si-containing substance in the powders ensures an *in situ* formation of the whiskers and the VS whisker formation process.

2 EXPERIMENTAL

2.1 Raw materials

The low cost nanometric amorphous Si–N–C powders for the whisker formation were synthesized by laser induced hexamethyldisilazane and ammonia vapor phase reactions. The synthesis method and the powder characteristics were reported elsewhere.[19] The powders used here have a mean particle diameter of 80 nm (obtained from TEM), are amorphous (identified by XRD), and have the composition of Si:50 wt%, N:28 wt%, C:15 wt%, and O:5 wt% which came from the surface absorption of the powders to the water and oxygen in the air due to the extraordinary high specific area of the powders.

2.2 Whisker synthesis

The schematics of the whisker synthesis apparatus are shown in Fig. 1. The Si–N–C powder was first slightly cold-pressed into several discs in order to avoid the powders being pumped out during evacuation of system. Each disc weighs 1 g, is 10 mm in diameter and 5 mm thick. The powder disc was placed in the BN crucible which was located in the graphite resistance furnace. The system was evacuated to a vacuum of 1·3 Pa, followed by the introduction of 1 atm of nitrogen into the furnace. Then, the sample was heated at a rate of 20 K/min to a defined temperature, kept constant for one hour, then cooled to room temperature by cutting off the electricity. Several runs were tried following this process at different synthesis temperatures between 1673K and 1973K at 100K intervals. Experiments using 1 atm of Ar instead of the nitrogen and using nanometric amorphous Si_3N_4 powders to replace the Si–N–C were also carried out in order to understand the whisker formation mechanism.

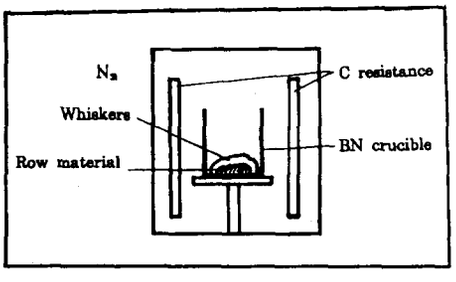

Fig. 1. Schematic diagram of whisker synthesis apparatus.

2.3 Characterization

The as-synthesized whiskers were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and FTIR techniques. XRD was performed on Philipps S/max-rA system using CuKα radiation by placing the whisker sample on the single crystal Si support plate. TEM was carried on Perkin TEM-420 equipment using an amorphous C sprayed Cu grid by dripping the methane to devolve whisker dispersion on the grid. Niclone 51-P IF-IR spectrometry was used to measure the IR spectrum of the whiskers after pressing the mixture of the whiskers and KBr into a small pellet.

3 RESULTS

3.1 Whisker formation conditions

White wool-like whiskers with a depth of 2 mm were observed on the annealed Si–N–C powder compact at 1873K in N_2. No whisker was found on the wall of the BN crucible of the graphite resistance heating body. Under the whiskers, there

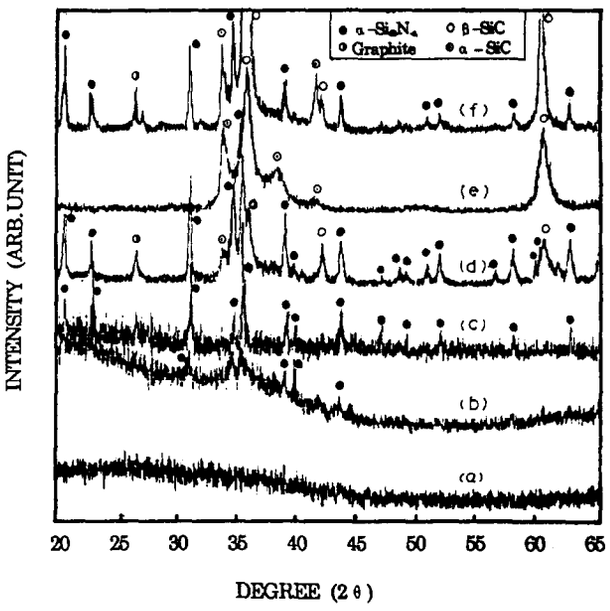

Fig. 2. XRD patterns of the Si_3N_4 whiskers (c), and the annealed products under 1 atm N_2 at (a) 1673K, (b) 1773K, (d)1873K, (f) 1973K, and (e) 1 atm Ar at 1873K.

existed a crystallized core. There was no whisker formation under these conditions: 1773K, and 1973K in N_2, 1873K in 1 atm Ar, and using amorphous Si_3N_4 powders as a raw material. The whisker formation temperature of 1873K was higher than that of 1623K at 1 atm N_2 in the SiO_2–C system. This indicates that the whiskers only formed under specific conditions satisfying both the phase stability and the supersaturated ratio of the gases via the whisker formation (see Discussion section).

XRD patterns of the crystallized phase under the different conditions, as well as the whiskers, are shown in Fig. 2. From Fig. 2 we can see that the whiskers are α–Si_3N_4 with no other crystallized phases such as SiO_2, C, or SiC in the whiskers. The crystallized core under the whiskers contained α–Si_3N_4, α and β–SiC, and graphite C, all of which are also the crystallized phases formed at 1973K, but the amount of SiC was increased. Only β–SiC was formed at 1873K in 1 atm Ar gas. Also, only α–Si_3N_4 was formed under 1 atm N_2 at 1773K, at which the amorphous powders began to crystallize. It was also found that in the case of using pure amorphous Si_3N_4, the obtained phases are a mixture of α and β-Si_3N_4 (not shown in Fig. 2).

3.2 Morphologies of the whiskers

A STEM picture of the whiskers is shown in Fig. 3. In most cases, the whiskers were found to be straight and long [Fig. 3(a)] although some bending whiskers were also present [Fig. 3(b)]. The mixture of α–Si_3N_4 grains and the shorter whiskers was found near the powder compact [Fig. 3(c)]. STEM observation showed that both the straight whiskers and the bending whiskers were generally several millimeters long and 0·5 μm in diameter.

TEM observation mainly gave four types of the whiskers: the thick straight whiskers with hexahedron cross section, the ribbon-like whiskers generally coiled with dislocations on one side, the prismatic whiskers with triangular cross sections, and the knuckled shorter whiskers, as shown in Fig. 4. All of these types of whiskers were of α–Si_3N_4, as proved by electron diffraction. The straight and thick whiskers and the ribbon-like whiskers all have a growth direction vertical to the (1101) plane, as the electron diffraction calibration of the growth direction shows in Fig. 4(c). This growth direction is the same as that observed by Wang and Wada.[12] Figure 4(b) is the dark field picture of Fig. 4(a), which shows perfect crystals on the outer layer of the whiskers, but a large amount of dislocation existed inside the whiskers.

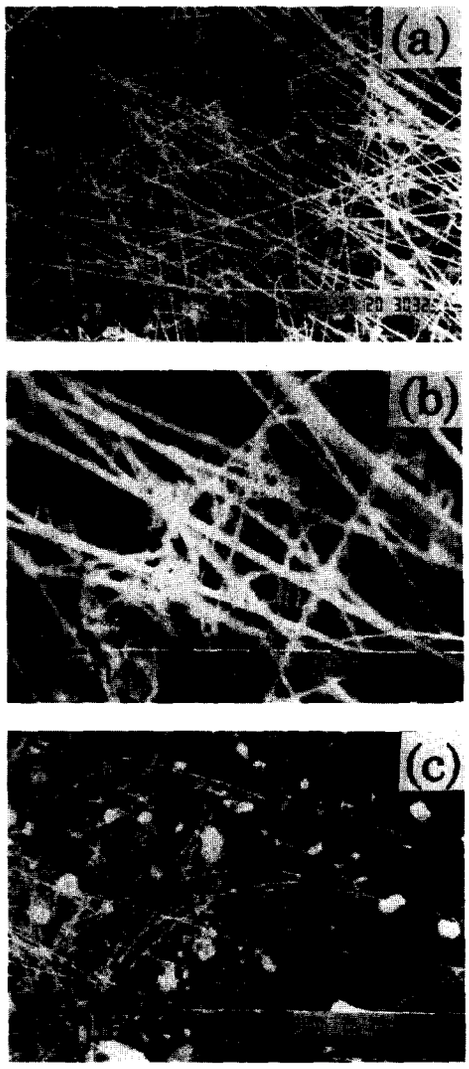

Fig. 3. STEM morphologies of the as-produced whiskers on (a) the outer layer, and (b) those near the Si–N–C compact.

TEM observation showed, that as no spherical droplet existed on the whisker tip and the tip seemed to be very smooth as shown in Fig. 5(a), that was not the whisker fracture since the fracture tip is generally much coarser under TEM observation. However, there can often be seen a small crystal bonded on the whisker tip as shown in Fig. 5(b) which is evidently the initial site of the whisker growth, since the small crystal is α–Si_3N_4 rather than the spherical amorphous droplet formed by the VLS whisker growth mechanism.[20] This indicates the whiskers grew on the α–Si_3N_4 grains crystallized from the Si–N–C powders. The grains only bonded to one side on the whisker end and there existed a larger number of dislocations in the other side. It is clear that the whiskers grew rapidly along the (1101) plane to form perfect crystals, followed by a slow thickening along the direction perpendicular to the growth direction to induce a lot of the dislocations in this side.

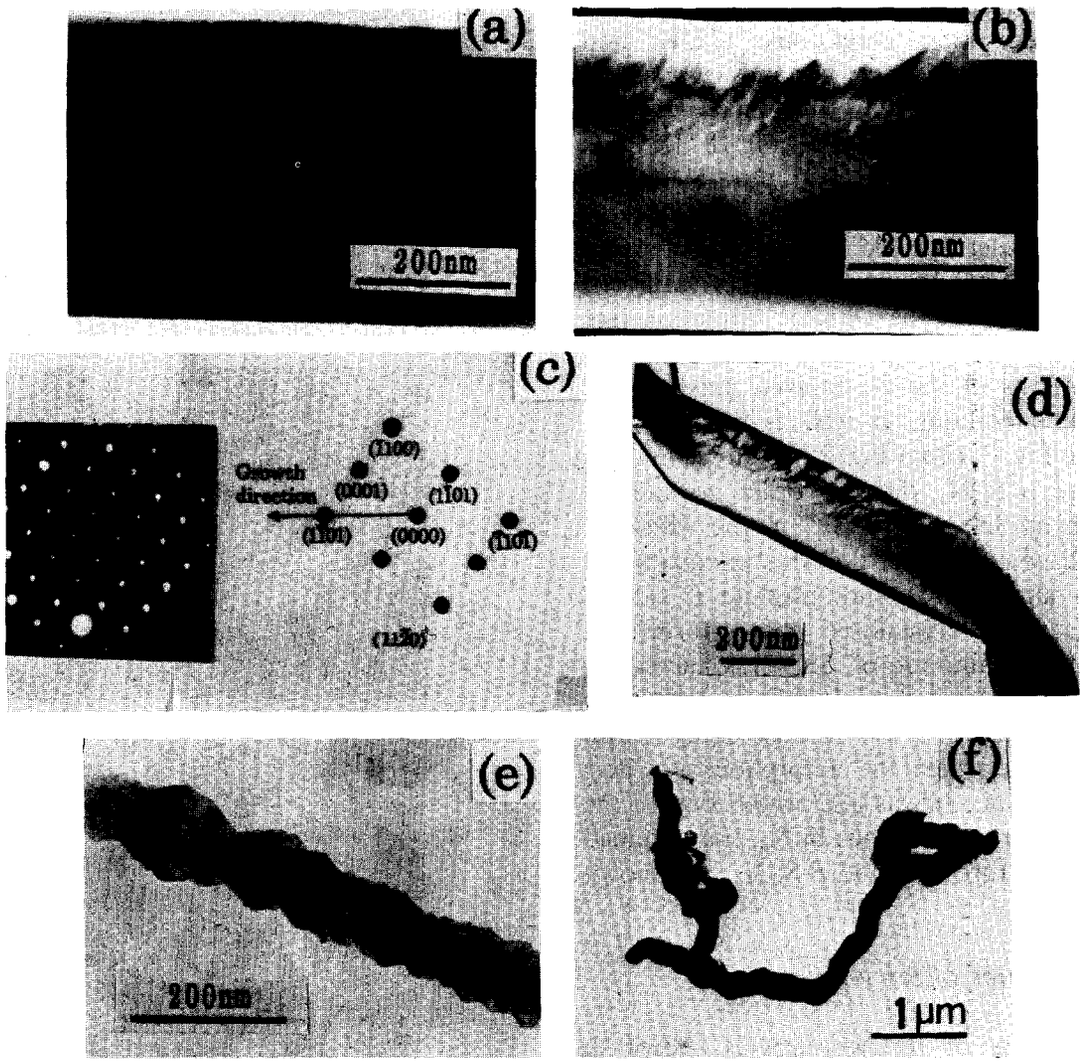

Fig. 4. TEM morphologies of the Si_3N_4 whiskers : (a) the straight whiskers, (b) the dark field picture of (a), (c) the growth direction calibration of the whiskers in (a), (d) the ribbon-like whiskers, (e) the prism-like whiskers with triangular cross section, (f) the knuckled whiskers.

3.3 FTIR spectrum of the whiskers

The FTIR spectra of the whiskers and the crystallized substance under the whiskers, namely Si_3N_4–SiC, is shown in Fig. 6, from which it can be seen that both spectra have a broad strong absorption peak centered at 950 cm^{-1}, but the peak of the Si_3N_4–SiC is wider than that of the whiskers. The broader absorption is believed to be caused by the coexistence of Si_3N_4 and SiC, both of which have strong characteristic vibration between 700 cm^{-1} and 1100 cm^{-1}, and the overlaps of the Si–N and Si–C in this region or possibly the existence of N–Si–C bond[21] resulted in the broad absorption peaks.

Another predominant difference between the two spectra is the appearance of many small absorptions in the lower wavenumber region and the

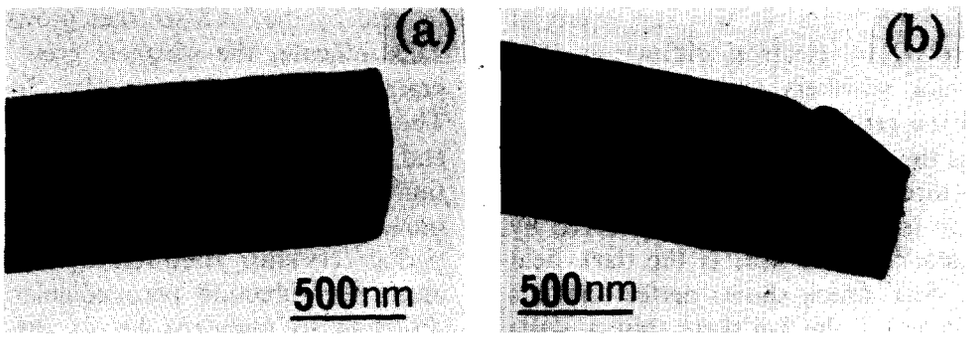

Fig. 5. TEM morphologies of the Si_3N_4 whisker tips: (a) the smooth whisker tip, (b) the whisker growth on the small α-Si_3N_4 grain.

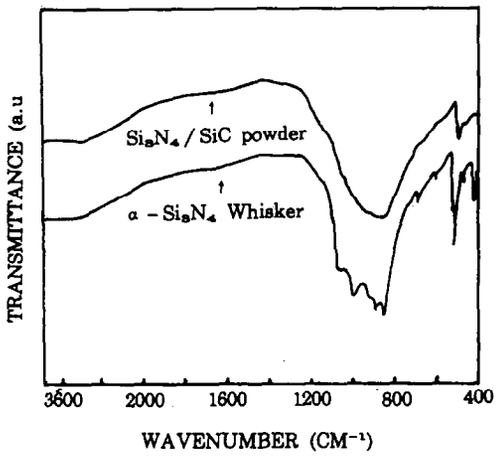

Fig. 6. FTIR spectra of the whiskers and the annealed products at 1873K under 1 atm N_2.

predominant peak splitting of the broad strong absorption for the whiskers. The absorption at 415, 470, 500, 510, 605 and 690 cm^{-1} for the whiskers are all assigned to the characteristic vibrations in α–Si_3N_4,[22] but no absorption appeared at 570 cm^{-1}, which is considered to be related to β–Si_3N_4,[23] indicating the absence of the β phase in the whiskers.

It is noted that the split of the broad absorption centered at 950 cm^{-1} for the whiskers results in four absorptions at 1050, 980, 880 and 840 cm^{-1}, which are also ascribed to the reported absorption for α–Si_3N_4,[22] but the absorption intensities at 1050 and 980 are lower than those at 880 and 840 cm^{-1} which is different from the generally observed intensity relationships among these peaks.[22] The absorption style is very similar to that of polycrystal Si_3N_4 obtained by Lin and Lee who found the absorption between 900 and 1050 cm^{-1} resulted from the reststrahlen effect.[23] The absorption at 1050 cm^{-1} was also ascribed to Si–O vibration due to the general existence of a layer of SiO_2 on the Si_3N_4 materials, such as the presence of the SiO_2 layer on the β–Si_3N_4 whiskers,[16] since the SiO_2 is a more stable phase in the ambient condition.

4 DISCUSSION

Obviously, the formation of the Si_3N_4 whiskers is related to the phase stability and the supersaturated ratio of the gases involved, such as SiO and CO/CO_2 which are important for the formation of Si_3N_4 powders[24] or whiskers[12] in the SiO_2–C–N_2 system. Since Si–N–C powders are metastable and liable to release CO and SiO during the crystallization of the powders due to the presence of absorbed O on the powder surface and the reaction of the gases with N_2 to form Si_3N_4 according to the generally accepted reaction (1)[12,24]

$$3SiO(g) + 3CO(g) + 2N_2(g) \text{----} Si_3N_4(s) + 3CO_2(g) \quad (1)$$

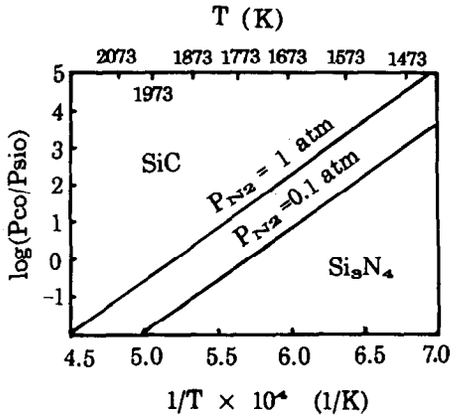

Fig. 7. Influence of P_{CO}/P_{SiO} ratio on the Si_3N_4/SiC equilibrium temperature under different P_{N_2}.

Since the whisker only formed at 1873K under 1 atm N_2, it is believed that a proper partial pressure of SiO and CO was attained under these conditions and the whisker nucleated on the preformed α–Si_3N_4 on the sample to grow along the {1101} plane.

It is generally known that there existed an upper limit temperature for reaction (1) for the formation of Si_3N_4, beyond which SiC would form by the reaction (2)[24]

$$SiO(g) + 2CO(g) = SiC(s) + CO_2 \quad (2)$$

However, the synthesis temperature of 1873K for whiskers is much higher than the generally measured upper temperature limit (around 1673K) for Si_3N_4 formation from a solid mixture of SiO_2+C for the reaction $3SiO_2(s)+6C(s) + 2N_2(g) = Si_3N_4(s)+6CO(g)$, for instance, which is 1673K for Si_3N_4 powder[24] and 1623K for Si_3N_4 whisker synthesis[12] for the same reaction system. It is therefore necessary to consider the equilibrium of Si_3N_4 and SiC via the gas phase reactions.

Combining reactions (1) and (2), we obtain the equilibrium reaction (3) between Si_3N_4 and SiC

$$3SiC(s) + 3SiO(g) + 4N_2(g) = 2Si_3N_4(s) + 3CO(g) \quad (3)$$

$$\log k_3 = \log (a^2_{Si_3N_4}/a^3_{SiC}) + 3 \log P_{CO} - 3 \log P_{SiO} - 4 \log P_{N_2} = 86663/T - 45{\cdot}12 \quad (3a)$$

where the equilibrium constant was calculated from the related values reported in Ref. 12 and it was assumed that $a^2_{Si_3N_4}/a^3_{SiC} = 1$ when both Si_3N_4 and SiC were in equilibrium. The influence of P_{CO}/P_{SiO} and P_{N_2} on Si_3N_4/SiC equilibrium temperature is plotted according to the relation (3a) in Fig. 7.

From Fig. 7, we can see that the equilibrium temperature increases with the decreasing P_{CO}/P_{SiO} ratio. This suggests a higher Si_3N_4 formation temperature should be used when the P_{CO}/P_{SiO} ratio is lower in the system. It is thought that the P_{CO}/P_{SiO}

ratio in the Si–N–C system is lower than that in the SiO_2—C system, since C is bonded to both Si and N atoms in the amorphous state in the former case, rather than in the free state. This is because the CO gas generation first needed the exceeded solid C release during the solid crystallization of SiC and Si_3N_4 from the Si–N–C matrix, which was a more dynamically controlled process. Also, it is seen that the reduction of P_{N_2} greatly decreases the upper limit temperature, which explains the formation of SiC only under 1 atm Ar at 1873K.

5 CONCLUSIONS

(1) High purity α–Si_3N_4 whiskers can by synthesized from amorphous Si–N–C powders at 1873K under 1 atm N_2. The whiskers exhibit straight, thick, ribbon-like, prism-like, or nodulated morphologies.

(2) The whiskers formed by the VS mechanism, by the reaction between N_2, SiO and CO which are released from the Si–N–C powders during heating. The whiskers nucleated on the preformed small Si_3N_4 grains in the Si–N–C compact along the {1101} plane, which ensures the *in situ* whisker formation.

(3) The Si_3N_4 whisker formation from the amorphous Si–N–C had a higher synthesis temperature compared with that from the solid mixture of the SiO_2 and C system. This is due to the lower P_{CO}/P_{SiO} in the Si–N–C case which resulted in the higher Si_3N_4 and SiC equilibrium temperature via the related gas phase reactions between SiO, CO and N_2.

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