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Short communication

Rapid crystallization of amorphous silicon nitride powder accelerated by liquid Si

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Abstract

The complete crystallization time of amorphous silicon nitride powder could be reduced from more than 6 h to 30 min by adding Si powder in N_2 atmosphere. The crystallization process may be affected by the synergy of the reaction between Si and N_2 and the liquid phase of Si due to the addition of Si. The α-Si_3N_4 produced by the added Si and nitrogen may be the seed of the crystallization process. The amorphous silicon nitride powder may be dissolved in the liquid phase and then precipitated as α-Si_3N_4. This article uses Ar instead of N_2 to shield the reaction between Si and N_2 in order to analyze the role of the two mechanisms. The added Si powder accelerates the crystallization process effectively in Ar. Powder of more than 70% crystalline phase content is produced by adding 5% Si annealing at 1400 °C for 15 min. The existence of liquid Si is the key factor to promote the crystallization process and the process follows the solution–precipitation mechanism. The final products are mainly α-Si_3N_4 and Si_2N_2O. The SEM results show that most of the products are irregular rod-like particles.

Keywords: Amorphous silicon nitride; Crystallization; SEM; XRD

1. Introduction

Silicon nitride ceramics have been widely used in the field of energy, metallurgy, machinery and aerospace industries [1–3]. The quality of the silicon nitride powder directly affects the performance of ceramic productions. Due to its high crystallization energy, nanosized amorphous silicon nitride powder of high surface energies offer significant advantages in terms of sintering rate [4–6]. Dense ceramics of more than 90% crystalline phase content are produced by direct sintering of unannealed amorphous powder at temperatures in the range of 1600–1800 °C [7–10]. During the sintering procedure of amorphous silicon nitride, there are a complex crystallization and phase transition: amorphous silicon nitride → equiaxial α-Si_3N_4 → equiaxial β-Si_3N_4 → rod-like Si_2N_2O → needle-like β-Si_3N_4 [8]. The amorphous silicon nitride powders exhibite larger shrinkage compared with crystallized ones [11]. The local densification and the formation of clusters happen during sintering connected with the crystallization process [12].

High quality silicon nitride ceramics are usually produced from pure silicon nitride powder of high α phase content with particle size in the micrometer range and a narrow particle size distribution. Synthesis of nanocrystalline materials from amorphous solids has been proposed for many years [13–15]. The crystallization of nanosized amorphous silicon nitride powder is one of the methods to produce sub-micron/nanosized α-Si_3N_4 powder. In the past two decades, several studies on the crystallization process of amorphous silicon nitride powder [16–19] and thin films [20] have been performed. Micrometer amorphous silicon nitride powder is prepared by pyrolysis of polysilazane under flowing NH_3 atmosphere, and nanosized amorphous silicon nitride powder is prepared by the vapor-phase reaction of silicon tetrachloride with ammonia. During the crystallization process of micrometer amorphous silicon nitride powder, the chlorine impurities inhibit grain growth, resulting in a delay of the initiation of crystallization. The activation energy calculated using a modified Avrami-Erofe'ev equation is 306 kJ/mol with chlorine impurities and 318 ± 45 kJ/mol without chlorine impurities [17,18]. The ammonium chloride impurities in the silicon nitride powder and the nitrogen in the furnace

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atmosphere cause the formation of whiskers [16]. A powder of about 80% crystalline phase content with an α/β ratio of about 6 is produced by annealing nanosized amorphous silicon nitride powder at 1450 °C for 360 min in nitrogen flow [19].

However, in earlier researches, the crystallization process of amorphous silicon nitride is very time consuming. The application of this method is still limited by the long crystallization time, low output, and high cost. Developing a means to shorten the crystallization time is a topic of utmost importance from both a theoretical and practical point of view. In our early research, the complete crystallization time of amorphous silicon nitride powder could be reduced from more than 6 h to 30 min by adding Si powder in N_2 atmosphere [21]. However, the promotion mechanism of Si powder in the crystallization process is not clear. The aim of this work is to study the crystallization mechanism by using Ar instead of N_2 to shield the reaction between Si and N_2.

2. Experiments

The amorphous silicon nitride powder prepared by chemical vapor-phase reaction method was provided by Hefei Kaier Nanometer Energy & Technology Co., Ltd. with a particle size about 25 nm. The silicon powder was provided by Beijing Yuanchuang Meiye Co., Ltd. with a particle size about 2.7 μm. The SEM images of the amorphous powder and Si powder are shown in Figs. 1 and 2. The size distribution of the amorphous silicon nitride powder is uniform and the shape is spherical and aggregates. The size distribution of the silicon powder is uneven and the shape is irregular and loose, with apparent angular on the surface.

The amorphous powder and Si powder are dried in a vacuum oven for 8 h at 100 °C to remove the adsorbed vapor before crystallization process. The crystallization tests have been performed in a resistance furnace filled with Ar. The crystallization products are analyzed by SEM and XRD.

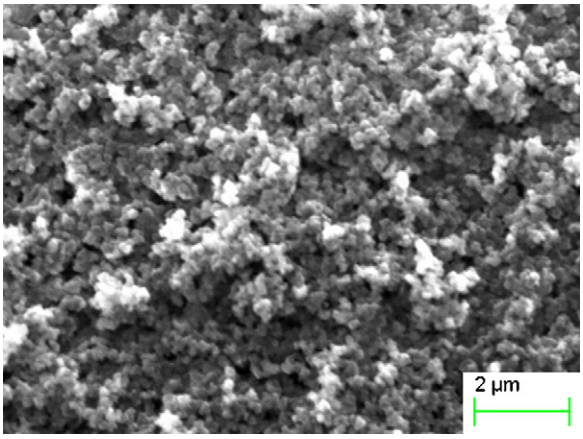

Fig. 1. SEM image of amorphous silicon nitride powder.

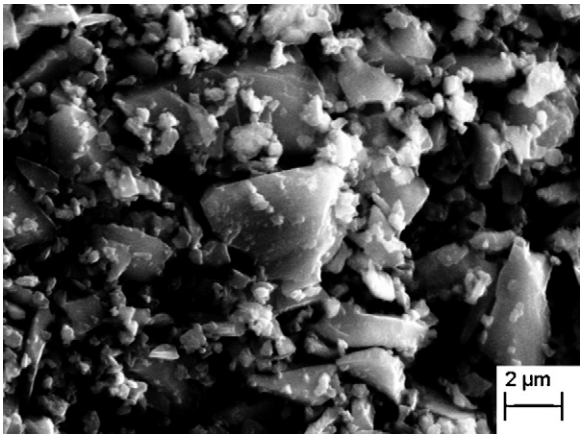

Fig. 2. SEM image of Si powder.

3. Results and discussion

Fig. 3 shows the XRD patterns of the products obtained after annealing pure amorphous silicon nitride powder at 1400 °C for 30 min and amorphous silicon nitride powder added with 5% Si

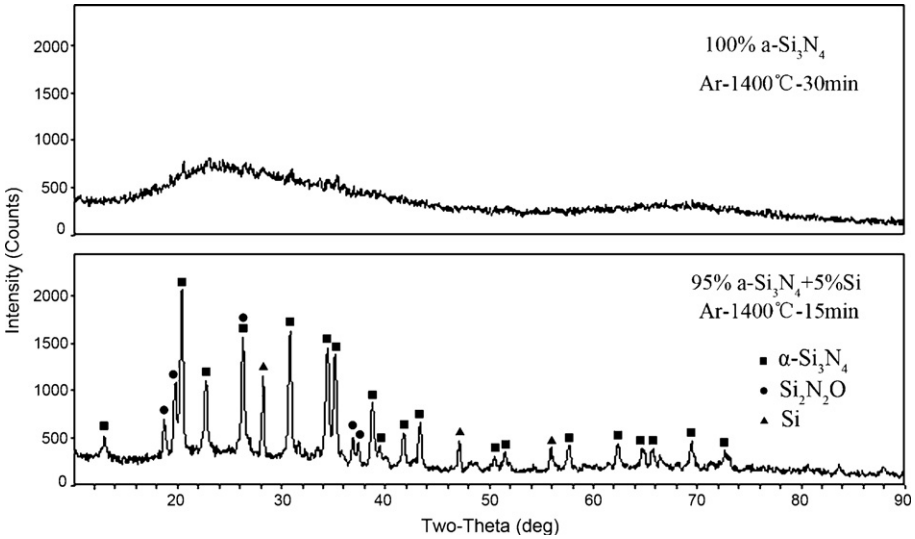

Fig. 3. XRD of the products obtained after annealing pure amorphous silicon nitride powder (a-Si_3N_4) for 30 min and amorphous powder added with 5% Si for 15 min at 1400 °C in Ar atmosphere.

at 1400 °C for 15 min in Ar atmosphere. The main peak of the product obtained after annealing pure amorphous silicon nitride is in a wide shape centered at about 25° which indicates that the main phase is amorphous. It can be inferred that the crystallization process of pure amorphous silicon nitride powder at 1400 °C in Ar atmosphere is very slow, and no obvious phase transformation can be observed after annealing for 30 min. It is similar to the result in N_2 atmosphere [21]. It can be judged that the effect of the atmosphere on the crystallization process of pure amorphous silicon nitride powder can be ignored. The main wide peak indicating amorphous phase centered at about 25° disappeared and the sharp peaks corresponding to the crystalline phase appeared in the product obtained after annealing amorphous powder added with 5% Si. It can be judged that the original amorphous powder has transformed to crystalline phases. The major phase of the crystallization product is α-Si_3N_4. Furthermore, Si_2N_2O has been formed because of the oxygen content in the starting amorphous silicon nitride powder (11.4%). The peaks of added Si can also be observed in the diffractogram. It can be inferred that the crystallization process of amorphous silicon nitride powder could be accelerated by adding Si powder. Powder of about 75% crystalline phase content is produced by adding 5% Si annealing at 1400 °C for 15 min.

The added Si powder could accelerate the crystallization process and reduce the crystallization time effectively in both N_2 [21] and Ar atmosphere. The products are mainly composed of α-Si_3N_4 and Si_2N_2O. However, the role of Si powder is different in the two kinds of atmosphere. The SEM image of the product obtained after annealing amorphous silicon nitride powder added with 5% Si in N_2 atmosphere for 15 min at 1450 °C is shown in Fig. 4. It is evident that most of the crystallization products are in the morphologies of columnar (A), whisker (B) and cluster (C) and some are spherical particles (D). The formation mechanisms of the products with different morphologies are different. The SEM image of the product obtained after annealing amorphous silicon nitride powder added with 5% Si in Ar atmosphere for 15 min at 1450 °C is shown in Fig. 5. It is evident that most of the

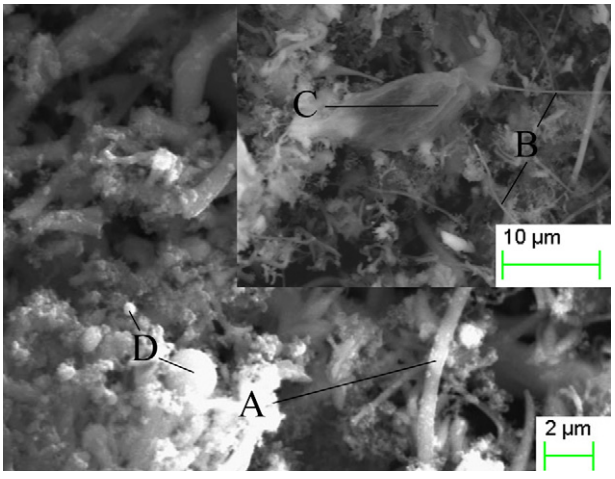

Fig. 4. SEM image of the product obtained after annealing amorphous silicon nitride powder added with 5% Si for 15 min at 1450 °C in N_2 atmosphere.

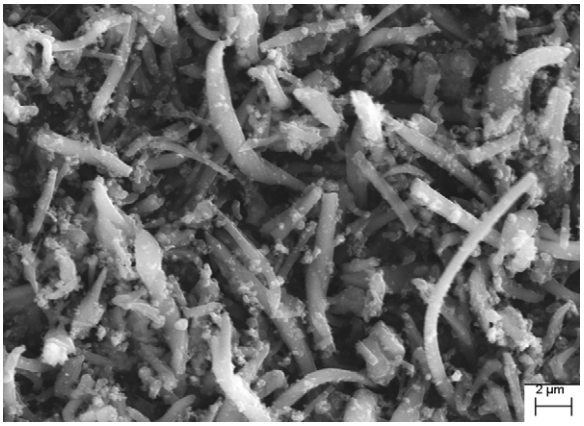

Fig. 5. SEM image of the product obtained after annealing amorphous silicon nitride powder added with 5% Si for 15 min at 1450 °C in Ar atmosphere.

crystallization products are in the morphologies of irregular rod-like particles. The formation mechanisms of the products with similar morphologies are same. The crystal grows well after 15 min annealing and a small amount of residual amorphous silicon nitride attaches to the crystal surface.

The liquid phase of Si has formed at the temperature higher than 1350 °C due to the alloy impurities. All reactions involved are shown as follows:

$$\text{Amorphous-}Si_3N_4(s) \rightarrow \alpha\text{-}Si_3N_4(s) \quad (1)$$

$$Si(s) \rightarrow Si(l) \quad (2)$$

$$3Si(s/l) + 2N_2(g) \rightarrow \alpha\text{-}Si_3N_4(s) \quad (3)$$

$$4Si_3N_4(s) + 3O_2(g) \rightarrow 6Si_2N_2O(s) + 2N_2(g) \quad (4)$$

The above four reactions will occur in the crystallization process in N_2 atmosphere and the crystallization may be affected by the synergy of the reaction between Si and N_2 and the liquid phase of Si. The α-Si_3N_4 produced by the added Si powder and nitrogen may be the seed of the crystallization process. And the amorphous silicon nitride powder may be dissolved in the liquid phase and then precipitated as α-Si_3N_4. The reaction between Si and N_2 can be shielded without reaction (3) in Ar atmosphere. The difference in the crystallization process between pure amorphous powder and the amorphous powder added with Si is whether reaction (2) occurs. So it can be inferred that the existence of liquid Si is the key factor to promote the crystallization process. The crystallization process without liquid Si is very slow. Due to the existence of liquid Si, the amorphous powder would be dissolved in the liquid phase and then precipitated as α-Si_3N_4. The mechanism of phase transformation from amorphous to crystalline can be explained as solution–precipitation mechanism.

4. Conclusions

In this paper, the crystallization process of amorphous silicon nitride powder in Ar atmosphere has been investigated

and compared with the process in N_2 atmosphere. The crystallization process of pure amorphous silicon nitride powder at 1400 °C in Ar atmosphere is very slow, and no obvious phase transformation can be observed after annealing for 30 min. Powder of more than 70% crystalline phase content is produced by adding 5% Si annealing at 1400 °C for 15 min. The crystalline phases are dominated by α-Si_3N_4 and Si_2N_2O. Most of the products obtained in N_2 atmosphere are in the morphologies of columnar, whisker and cluster and some are spherical particles. Most of the products obtained in Ar atmosphere are in the morphologies of irregular rod-like particles. The existence of liquid Si is the key factor to promote the crystallization process. The process follows the solution–precipitation mechanism.

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References

[1] F.L. Riley, Silicon nitride and related materials, J. Am. Ceram. Soc. 83 (2) (2000) 245–265.
[2] R.N. Katz, Applications of silicon nitride based ceramics, Ind. Ceram. (Italy) 17 (3) (1997) 158–164.
[3] A. Okada, Automotive and industrial applications of structural ceramics in Japan, J. Eur. Ceram. Soc. 28 (5) (2008) 1097–1104.
[4] M. Ziegler, H. Heinrich, G. Wöttig, Relationships between processing, microstructure and properties of dense and reaction-bonded silicon nitride, J. Mater. Sci. 22 (1987) 3041–3086.
[5] M. Mitomo, Thermodynamics, phase relations and sintering aids of silicon nitride, in: S. Somiya, M. Mitomo, M. Yoshimura (Eds.), Silicon Nitride-1, Elsevier, London, 1990, pp. 1–12.
[6] J. Szépvölgyi, F.L. Riley, I. Mohai, I. Bertóti, E. Gilbart, Composition and microstructure of nanosize, amorphous and crystalline silicon nitride powders before, during and after densification, J. Mater. Chem. 6 (1996) 1175–1186.
[7] J. Luo, R. Luo, Effect of additives on the sintering of amorphous nano-sized silicon nitride powders, J. Wuhan Univ. Technol. Mater. Sci. Ed. 24 (4) (2009) 537–539.
[8] J. Luo, K. Zhang, G. Wang, W. Han, Fabrication of fine-grained Si_3N_4–Si_2N_2O composites by sintering amorphous nano-sized silicon nitride powders, J. Wuhan Univ. Technol. Mater. Sci. Ed. 21 (3) (2006) 97–99.
[9] G.T. Burns, J.A. Ewald, K. Mukherjee, Hot-press sintering studies of amorphous silicon nitride powders, J. Mater. Sci. 27 (1992) 3599–3604.
[10] Y. Moriyoshi, M. Futaki, N. Ekinaga, T. Nakata, Sintering and microstructure of silicon nitride prepared by plasma CVD, J. Mater. Sci. 27 (1992) 4477–4482.
[11] C. Gomez-Aleixandre, J.M. Albella, J.M. Martínez-Duart, F. Orgaz, Crystallization and sintering characteristics of chemically vapor deposited silicon nitride powders, J. Mater. Res. 7 (10) (1992) 2864–2868.
[12] H.T. Sawhill, J.S. Haggerty, Crystallization of ultrafine amorphous Si_3N_4 during sintering, J. Am. Ceram. Soc. 65 (8) (1982) c131–c132.
[13] H. Gleiter, Nanocrystalline materials, Prog. Mater. Sci. 33 (4) (1989) 223–315.
[14] R. Birringer, U. Herr, H. Gleiter, Nanocrystalline materials—a first report, Trans. Jpn. Inst. Met. Suppl. 27 (1986) 43–52.
[15] K. Lu, Synthesis of nanocrystalline materials from amorphous solids, Adv. Mater. 11 (13) (1999) 1127–1128.
[16] F. Allaire, R. Langlois, Factors influencing the crystallization of ultrafine plasma-synthesized silicon nitride as a single powder and in composite SiC–Si_3N_4 powder, J. Mater. Sci. 27 (1992) 1265–1270.
[17] R. Riedel, M. Seher, Crystallization behaviour of amorphous silicon nitride, J. Eur. Ceram. Soc. 7 (1991) 21–25.
[18] M. Seher, J. Bill, F. Aldinger, R. Riedel, Crystallization kinetics of polysilazane-derived amorphous silicon nitride, J. Cryst. Growth 137 (1994) 452–456.
[19] J. Szépvölgyi, I. Mohai, Crystallization of an amorphous silicon nitride powder produced in a radiofrequency thermal plasma, Ceram. Int. 25 (1999) 711–715.
[20] N. Jehanathan, M. Saunders, Y. Liu, J. Dell, Crystallization of silicon nitride thin films synthesized by plasma-enhanced chemical vapour deposition, Scr. Mater. 57 (2007) 739–742.
[21] Y. Li, L. Wang, S. Yin, F. Yang, P. Wu, Rapid crystallization process of amorphous silicon nitride, J. Am. Ceram. Soc. 94 (12) (2011) 4169–4173.