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Preparation of nano aluminum nitride powders by polymer network method

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In this work, aluminum nitrate (Al(NO₃)₃), active carbon and $C_{12}H_{22}O_{11}$ were used as raw materials. The nano aluminum nitride powders (AlN) were synthesis by polymer network method. Aluminum nitride (AlN) exhibits high thermal conductivity, low dielectric permittivity and good electric insulativity. It has a very high synthetic temperature, however, results in a high cost. The aim of this investigation is to develop a new method of fabricating ultra-fine AlN powders to lower the synthetic temperature of AlN. The influences of different carbon sources and the synthetic temperature on fabricating AlN powders via polymer network method were investigated, and the mechanism of AlN formation was also identified. The results indicated that as using sucrose ($C_{12}H_{22}O_{11}$) as the carbon source, the optimum synthetic process condition for fabricating ultra-fine AlN powders was at 1500 °C for 2 h. Comparing with the mechanical ball-milling method, the temperature of synthesizing AlN powders was lowered about 100 °C. Furthermore, the size of as-synthesized AlN was finer from 50 nm to 80 nm.

Key words: Polymer network structure, Aluminum nitrate, Polymer network method, Synthesis methodIntroduction.

Introduction

Aluminum nitride (AlN) ceramic, as an ideal electronic substrate material, has attracted more attention in the electronic industry due to its excellent properties such as high thermal conductivity, low dielectric permittivity, good electric insulativity, thermal stability and the anti-corrosion. The purity and ultrafine size of powders, as the important performance indexes in evaluating electronic substrate materials [1], have great significance on thermal conductivity of materials. Therefore, there are many methods to fabricate AlN powders, such as the direct nitridation [2, 3], the high-energy ball milling [4, 5], the plasma gasification method [6-8] and the sol-gel method [9]. Through using the direct nitridation method [10], the quality of AlN powders is difficult to be controlled due to the self-sintering behavior of powders. Besides, by using the high-energy ball milling method, the original powders are easily being polluted which results in a low purity [11]. The synthesis temperature on plasma gasification method is quite high, and agglomeration happened as using sol-gel method. In this paper, not only would the polymer network method have a low cost, but could make various components distributed uniformly in gel structure [12, 13]. In addition, the gel structure of polymer network could prevent the agglomeration of colloidal particles and the emergence of layered phenomenon from being caused by the

difference of specific gravity between raw materials in the AIN precursors. Aluminum nitride synthesis temperature is lower. Its particle diameter is smaller. Therefore, the polymer network method could be as a simple and efficient method to prepare the high-purity and ultra-fine AIN powders with a lower cost. Furthermore, it is reported that there is little information about the preparation of AIN nano powders by polymer network method. Therefore, this study has a certain innovation and practical application value.

Experimental Procedures

In this work, aluminum nitrate $(Al(NO_3)_3)$, active carbon and $C_{12}H_{22}O_{11}$ are used as raw materials. Besides, acrylamide (C_3H_5NO) , N,N-methylene bis acrylamide $(C_7H_{10}N_2O_2)$, ammonium persulfate $((NH_4)_2S_2O_8)$ are used as polymerization monomer, cross-linking agent, initiating agent, respectively.

Firstly, according to a certain atom molar ratio between carbon(C) atom and aluminum (Al) atom (C : Al = 1 : 6), carbon sources ($C_{12}H_{22}O_{11}$ and active carbon) are added into Al(NO₃)₃ solution (molar concentration is 0.3 mol/L) and fully being dissolved. And then polymerization monomer, cross-linking agent and initiating agent with a mass ratio of 100 : 4 : 25 are added to the above solution. Then, the mixed solution is heated to 65 °C for 2 h with regularly stirring. Finally, a gel is formed. The obtained gel has been dried at 90 °C for 24 h in a drying oven and then grinded into powders. AlN precursors are acquired.

For making a contrast sample in this work, nano alumina (Al_2O_3) and active carbon are utilized as raw materials to fabricate AlN powders. Firstly, nano

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alumina (Al_2O_3) and active carbon are mixed for 36 h in an ethanol medium by mechanical ball-milling method. The mass ratio between ceramic grinding balls (zirconium dioxide (ZrO₂) balls) and raw materials is 5 : 1. The certain molar ratio between carbon (C) atom and aluminum (Al) atom is still 1 : 6 (C : Al = 1 : 6).

Then the above-mentioned AlN precursors is calcined for 2h at the different temperature levels of 1400 °C, 1450 °C, 1500 °C and 1600 °C within flowing N₂ atmosphere (8-10 L/min flow rate), respectively. Then, the as-synthesized powders are cooled to genera temperature. Next, the powders are being put into resistance furnace to remove residual carbon at 600°C for 3 h in air. Finally, AlN powders are synthesized. As well, in the mechanical ball-milling method, nano alumina (Al₂O₃) and active carbon have been put into carbon tube furnace to synthesize AlN powders via using the same thermal treatment process.

The morphology of AlN precursors has been examined by scanning electron microscope (SEM; SSX-550). The component analysis of AlN precursors is determined by using energy dispersive X-ray spectroscopy (EDS). The phase composition of the obtained AlN powders is identified via X-ray diffraction (XRD; PW3040/60) using CuK α radiation at 45 kV and 40 mA.

Results and Discussion

Under initiating agent $((NH_4)_2S_2O_8)$, the polymerization reaction among monomers (C3H5NO) is happened. Meanwhile, crosslink reaction is occurred via crosslinking agent ($C_7H_{10}N_2O_2$). Polymer network structure has been gotten. The mechanism of forming polymer network structure can be summarized in the following chemical reaction equations (1), (2) and (3) [14]. The primary radical has being generated through the thermal decomposition of initiator (Eq. (1)), subsequently, the polymerization reaction and the cross-linking reaction started (Eq. (2) and (3)). Finally, the polymer network structure was formalized. Among them, capital characters P and R represent $S_2O_8{}^{2-}$ and $SO_4{}^-$ separately from an initiator molecule. The asterisk (*) represents a primary radical. Capital characters M and X respectively are polymerization monomer (C₃H₅NO) and crosslinking agent (C₇H₁₀N₂O₂), and the lowercase characters of n or m in the above equations (2) and (3) are equated to 1, 2, 3 ----.

$$\begin{split} & P \rightarrow 2R^{*} \qquad (1) \\ & R^{*} + M \rightarrow R \ M^{*} \\ & R \ M^{*} + M \rightarrow R \ M_{2}^{*} \\ & R \ M_{2}^{*} + M \rightarrow R \ M_{3}^{*} \\ & \hline & R \ M_{n-1}^{*} + M \rightarrow RM_{n}^{*} \end{split}$$

$$RM_{m}^{*} + X + RM_{1}^{*} \rightarrow R[M]_{m}X[M]_{1}R$$
(3)



Fig. 1. The infrared spectrogram of three-dimensional polymer network.



Fig. 2. SEM images of AIN precursor prepared with different carbon source (a) Activated carbon; (b) Sucrose; (c) The magnification image of fig. 2(b); (d)EDS spectrum in point A.

Figure 1 represents the infrared spectrum of preparation aluminum nitride by polymer network. The stretching vibration absorption peaks of the groups CH_2 exist at 2803 cm⁻¹. At 3034 cm⁻¹, there is a stretching vibration absorption peak of NH₂ group from acrylamide monomer. The weak stretching vibration absorption peak for sulfate characteristic is appeared at 1045 cm⁻¹. It was further verified that the formation of threedimensional polymer network has been proceeding under the effect of initiator by monomer polymerization and cross-linking reaction

Fig. 2 shows the SEM images of AlN precursors which is prepared by polymer network method by using different carbon source (active carbon or $C_{12}H_{22}O_{11}$). When using active carbon as carbon source, as shown in Fig. 2(a), there is a obvious layered phenomenon. The reason is that the active carbon can not be dissolved in an aqueous solution and the difference of specific gravity between components results in the layered phenomenon. Utilizing $C_{12}H_{22}O_{11}$ as the carbon source, however, leads to no the layered phenomenon presentation in AlN precursors. This is because $C_{12}H_{22}O_{11}$ can be dissolved in an aqueous solution and the gel will



Fig. 3. XRD pattern by polymer network method.

be obtained, as shown in fig. 2(b). Fig. 2(c) shows the high-resolution SEM image of fig. 2(b), it indicates that the microstructure of gel is very uniform. Fig. 2(d) shows the EDS spectrum of point A in fig. 2(c). The presence of carbon (C), oxygen (O) and aluminum (Al) elements in gel demonstrat that the substances of carbon and aluminum source of AlN precursors are uniformly distributed in polymer network structure, And there is no a obvious layered phenomenon. Therefore, The atomic diffusion distance of synthesizing ultra-fine AlN powders is short.

Fig. 3 shows the XRD pattern of as-synthesized powders under different temperature levels for 2 h through the polymer network method. Fig. 3(a) shows the XRD pattern of as-synthesized powders at the temperature level of 1400 °C, it reveals that The (100), (101), (110) and (103) peaks of AlN phase could be observed, and the first (100) and second (101) highest intensity peaks are very weak and broad, which indicates that the as-synthesized AlN powders are in amorphous status. Furthermore, the diffractive peaks of aluminum oxynitride (AlON) phase, alumina (Al₂O₃) and carbon (C) also exist in the XRD patterns, which indicates that the formation process of AlN phase is in corresponding to two steps. Firstly, one is for generating intermediate AlON phase from Al₂O₃ phase under the flowing N₂ atmosphere, then, another step is for generating AlN phase from the intermediate AlON phase, as shown in chemical reactions (4) and (5) below. In other words, a portion of carbon atoms unite with oxygen atoms to form carbon monoxide gas, meanwhile, a portion of oxygen atom is replaced by nitrogen atoms to form an intermediate AlON phase. Then, the oxygen atom in intermediate AlON phase freshly generated is pulled out by carbon atom to finally form Aluminum nitride phase, as a result that the homogeneous distribution of carbon (C), oxygen (O) and aluminum (Al) elements in gel is of great crucial.

$$Al_2O_3 + C + N_2 \rightarrow 2AION + CO \tag{4}$$



Fig. 4. XRD pattern by mechanical ball-milling method.

$$AION + C \rightarrow AIN + CO$$
 (5)

When raising the temperature up to 1450 °C, as shown in fig. 3(b), the presences of the (111), (220), (400) and (333) diffraction peaks of AlON reveal that the phase transformation of AlN is still incomplete. There are no the typical diffraction peaks of Al₂O₃, which indicates that Al₂O₃ has been transformed into AlN and AlON completely. When the synthetic temperature has reached up to 1500 °C, as shown in fig. 3(c), the diffractive peaks of the intermediate phase AlON does not appear and only the typical diffraction peaks of carbon and AlN are taken on. The increasing intensity of the typical (100), (101), (110) peaks of AIN demonstrates that the transformation of AlN phase is approaching to full complete. Therefore, the optimum synthetic process for preparation of AlN powders by polymer network method should be set at 1500 °C for 2 h.

Fig. 4 shows the XRD patterns of the as-synthesized powders by mechanical ball-milling method under different synthetic temperatures for 2 h. In the XRD patterns at 1450 °C, as shown in fig. 4(a), the existence of the typical (100), (101) and (110) peaks of AlN shows that AlN phase has been formed. But these peaks are very weak and broad, which indicates that the as-synthesized AlN powders are in amorphous status. In addition, the presence of the diffraction peaks of Al_2O_3 and the no emergence of the AlON phase indicate that through using mechanical ball-milling method, the formation of AlN phase is a carbothermal reduction reaction [15] of Al_2O_3 , as shown in chemical reaction equation (6) as following.

$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO$$
 (6)

The intermediate phase AlON could hardly be formed when the operating temperature up to 1500 °C and 1550 °C, as shown in fig. 4(b) and fig. 4(c). When the temperature reaches up to 1600 °C, as shown in fig. 4(d), only the typical diffraction peaks of AlN phase



Fig. 5. SEM image of as-synthesized AlN powders by different synthesis methods (a) By polymer network method; (b) By mechanical ballmilling method.

appear in XRD pattern, and the intensity of the diffraction peaks of AlN is very high, which suggests AlN was formed completely. It implies that the optimum synthetic process of preparing AlN by mechanical mixing method is at 1600 °C for 2 h.

Synthesis method affects the forming temperature and particle diameter of nano aluminum nitride powders. Comparing fig. 3 with fig. 4, the synthesis temperature of preparing AlN with polymer network method is 100 °C lower than mechanical ball-milling method. Therefore, the size of AlN powder by the polymer network method is less than by mechanical ball-milling method, as shown in fig. 5 (a) and fig. 5 (b). It is also shown that the diameter of AlN powders by polymer network method is about 50-80 nm. Meanwhile, the diameter of AlN powders by mechanical ballmilling method is about 200-300 nm. The main reason is presumed that polymer network method could make aluminum (Al) sources and carbon (C) sources be distributed more uniformly, and that the potential barrier of forming aluminum nitride AlN owing to generating intermediate AlON phase is reduced immensely, so as conformity with above results. In addition, the polymer network framework could provide channels for the diffusion of nitrogen-atoms, which ensure a valid contact between nitrogen-atoms and reactants, hence the synthetic temperature of AlN powders will be lower.

Conclusions

In this study, a new polymer network method is employed to synthesize AlN powders successfully. As $C_{12}H_{22}O_{11}$ is selected as carbon source, the synthetic temperature of AlN powder could be remarkably lowered. The synthetic temperature is lowered about 100 °C than using mechanical ball-milling method. In addition, the diameter of AlN powders prepared by polymer network method is between 50 and 80 nm, which is much finer than that the one prepared by mechanical ball-milling method.

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References

- T. B. Jackson, A.V. Virkar, K.L. More, R.B. Dinwiddie, and R.A. Cutler, Am. Ceram. Soc. 80 (1997) 1421-1435.
- C.S. lung, Y.W. Liang, and L.C. Nan, Mater. Res. 14 (1999) 1928-1933.
- 3. S.M. Bradshaw, and J.L. Spicer, Am. Ceram. Soc. 82 (1999) 2293-2300.
- 4. A. Calka, J.I. Nikolov, and G.H.J. Wantenaar, Appl. Phy. 75 (1994) 4953-4955.
- B.L. Li, J.E. Zhou, and S.Q. Sheng, Journal of Inorganic Materials 21 (2006) 821-827.
- M. Akiyama, C.N. Xu, M. Kodama, I. Usui, K. Nonaka, and T. Watanabe, Am. Ceram. Soc. 84 (2001) 1917-1920.
- 7. K. Etemadi, Plasma Chemistry and Plasma Processing 11 (1991) 41-56.
- C. Balasubramanian, V.P. Godbole, V.K. Rohatgi, A.K. Das, and S.V. Bhoraskar, Nanotechnology 15 (2004) 370-373.
- M.L. Qin, X.H. Qu, J.L. Lin, P.A. Xiao, and B.J. Zhu, Materials Science and Engineering of Powder Metallurgy 7 (2002) 50-54.
- H.L. Zhu, and R.S. Averback, Materials and Manufacturing Processes 11 (1996) 905-923.
- A. Bruckmann, A. Krebs, and C. Bolm , Green Chem. 10 (2008) 1131-1141.
- H.Z. Wang, L. Gao, W.Q. Li, and Q. Li, Journal of Inorganic Materials 15 (2000) 356-360.
- C.H. Lee, S.Y. Hwang, J.Y. Sohn, H.B. Park, J.Y. Kim, and Y.M. Lee, Journal of Power Sources 163 (2006) 339-348.
- 14. A. Douy, P.Odier, Mater. Res. Bull. 24 (1989) 1119-1126.
- H.Y. Wei, D.S. Pei, Z.Y. Du, J.H. Zhao, Y.N. Wei, Y.B. Geng, R.S. Wang, and J.L. Bu, Advanced Materials Research 418-420 (2011) 342-345.