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Synthesis of aluminum nitride fibres from aluminum silicate fibres by carbothermal reduction method*

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Aluminum nitride (AlN) fibres were synthesized by carbothermal reduction of aluminum silicate fibres and carbon black in a flowing nitrogen atmosphere. XRD and SEM were employed to study the phase structure, chemical composition and morphologies of the products. It is suggested that aluminum silicate fibres can be converted into AlN fibres by carbothermal reduction. SEM confirmed that the fibres maintained the morphologies of aluminum silicate fibres during reduction, but their details of surface have been altered. A carbothermal nitriding model of the aluminum silicate fibres has been developed.

1. Introduction

Aluminum nitride has excellent potential for use as a substrate material for high-density, high-power, and high-speed integrated circuit applications. It exhibits high thermal conductivity, low thermal expansion mismatch relative to Si, high electrical insulation, high dielectric breakdown strength, good mechanical strength, ease of cutting and polishing, excellent chemical stability and nontoxicity [1]. Recently, there was much interest internationally in synthesis of aluminum nitride powders and fabrication of aluminum nitride ceramics. Meanwhile aluminum nitride fibres and whiskers have attracted much attention, as their perfect or near perfect crystal structure and higher thermal conductivity than polycrystal aluminum nitride ceramics [2]. At present the materials used as substrate and package of microelectronics mainly are alumina, polymer and glass, etc. The ceramics used as substrate and package have high thermal conductivity and low thermal expansion mismatch to Si, but its dielectric constant is too high for high-speed integrated circuits. The polymer-based materials used as substrate and package have unique advantage as their low dielectric constant and ease fabrication, but their thermal conductivity is too low to use broadly. Both of them are difficult to meet the need of high power integrated circuits package and very large scale integration (VLSI) substrate. Recent development indicated that a composite of ceramic fibres or whiskers with polymers could achieve an excellent property balance for electronics, the high thermal conductivity and stability of ceramics, coupled with the low dielectric constant and ease of processing of polymers [3, 4]. It was also indicated that the composite of AlN fibres or whiskers with polymers would promise such kinds of balance. The theory calculations for a quasi-isotropic composite of 50 vol % AlN fibres in Teflon fluoropolymer, predicted a composite with thermal conductivity 25–60 $W/m \cdot K$, coefficient of thermal expansion 4–$5 \times 10^{-6}/^{\circ}C$ (20–200 °C) and dielectric constant 2.8–5 (1 MHz) [5]. Whereas, the key problem affecting this technique to be used is how to synthesize or fabricate large mount of AlN fibres and whiskers at low cost. Along these lines, many researchers have already developed effective ways to synthesize and fabricate AlN fibres and whiskers. Up to now, among the methods used to synthesize or fabricate AlN fibres and whiskers [6], the most important and potential to commercial use were carbothermal reduction of Al_2O_3 and pyrolysis of thermoplastic organoaluminum precursor. In 1988 Bolt *et al.* developed a synthesized route to AlN with pyrolysis of thermoplastic organoaluminum [7]. Caceres and Zhou *et al.* respectively in 1994 and 1996 successful synthesized AlN whiskers using carbothermal reduction [8, 9]. Since the thermoplastic organoaluminum for pyrolysis to fabricate AlN fibres was very expensive, and the yield of AlN whiskers by carbothermal reduction was very low, it is necessary to develop a new method to synthesize AlN fibres or whiskers.

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In this paper, a new method has been developed to *in-situ* synthesize aluminum nitride fibres by carbothermal reduction method using aluminum silicate fibres and carbon black as the raw materials. This paper describes initial observations on AlN fibres from aluminum silicate fibres by carbothermal reduction, and the technical process of *in-situ* synthesized AlN fibres by carbothermal reduction of aluminum silicate fibres. XRD and SEM were employed to study the phase, chemical composition and morphologies of the products. A model of the carbothermal nitriding of aluminum silicate fibres has been developed.

2. Experimental

All carbothermal reduction experiments were carried out in a vertical, controlled-atmosphere and graphite element resistance furnace. Aluminum silicate fibres and black carbon were used in this study. Raw aluminum silicate fibres were chopped to produce suitable length fibres, slurry of carbon black was prepared by ultrasonic dispersion in ethanol. The chopped fibres were fed into the slurry and dispersed by ultrasonic stirring for 1h. The slurry with chopped fibres was filtered. The filtrate containing the fibres was dried in an oven at 60 °C for 24 h. By this treatment the aluminum silicate fibres were uniformly coated with carbon black. The dry coated fibres were placed in a graphite crucible of 2.5 mm wall thickness and the crucible was closed with a graphite lid and heat-treated in the graphite resistance heating furnace. Heat treatment of the coated aluminum silicate fibres was conducted at 1650 °C for 5 h in a flowing nitrogen atmosphere. The nitrogen flow rate was maintained at 0.6 l/min. The heating rate was 40 °C/min. A Rigaku X-ray diffractometer (DMAX IIIB) with Ni-filtered CuK_α radiation was used for X-ray diffraction (XRD) analysis. The synthesized products were decarburized at 700 °C in a conventional muffle furnace for 5 h. The remainder was considered to be AlN, the converted fibres were examined by scanning electron microscope (SEM, OPTON CSM950).

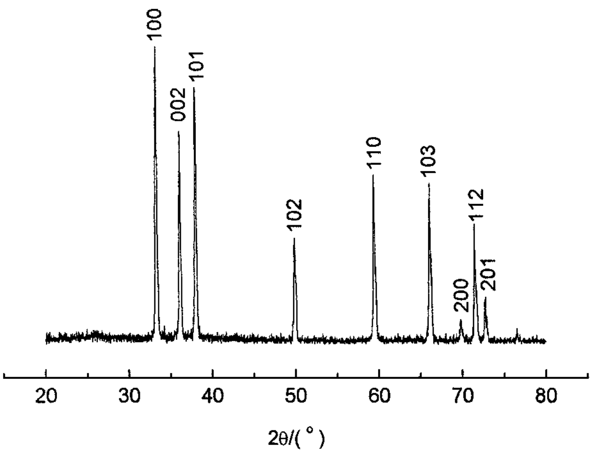

Figure 1 The X-ray diffraction pattern of AlN fibres.

3. Results and discussion

3.1. The X-ray diffraction analysis and SEM observation of the products

The XRD pattern of synthesized products is shown in Fig. 1. The XRD pattern confirmed that the only phase is AlN. SEM micrographs of aluminum silicate fibres and synthesized products are shown in Fig. 2. The aluminum silicate fibres was polycrystal with smooth

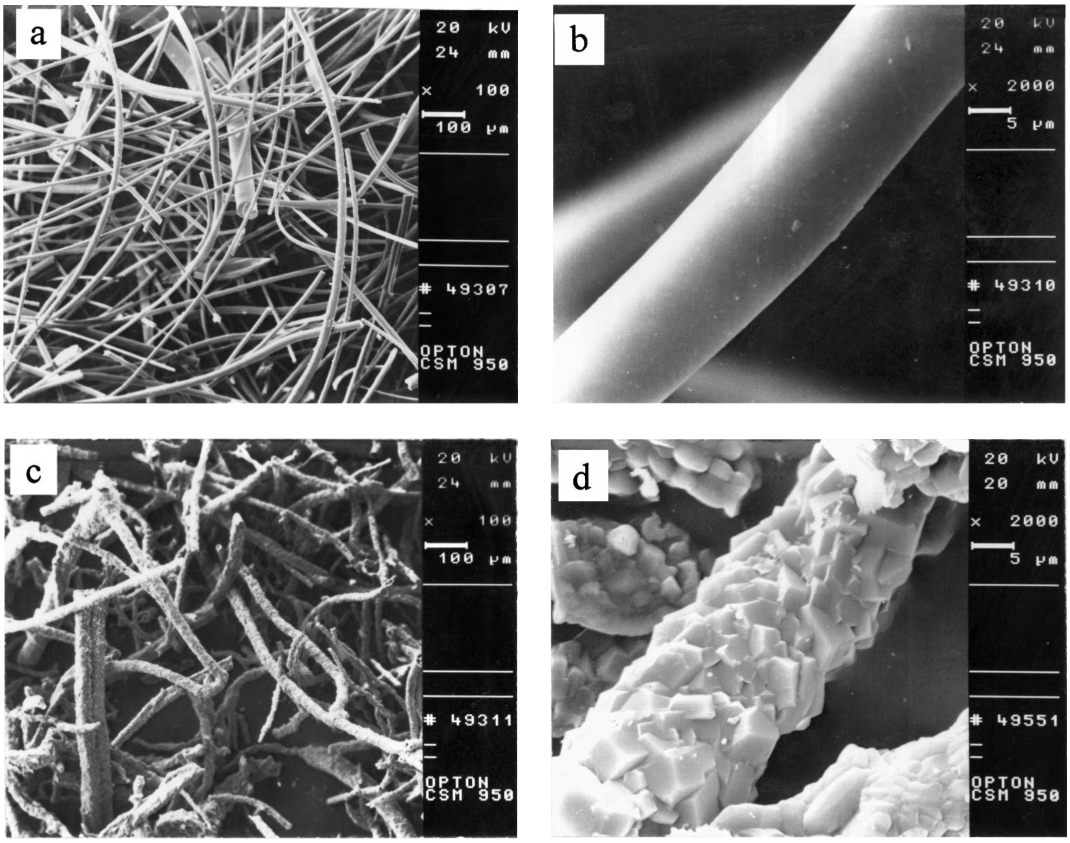

Figure 2 The SEM morphologies of aluminum silicate fibres and AlN fibres.

surface, their diameters range from 5 to 10 μm (Fig. 2a and b), and the synthesized products were polycrystal fibres with small grains in micrometers (Fig. 2c and d), and they retained the original aluminum silicate fibres morphology.

3.2. The mechanism and a model of AlN fibres formation

The aluminum silicate fibres were usually used as refractory materials and heat insulated materials. It has two kinds of amorphous fibres and polycrystal fibres. The polycrystal fibres were fixed compound composite with Al_2O_3 and SiO_2 [10]. In this study, the sillimanite fibres were used containing 62.92% Al_2O_3 and 37.08% SiO_2.

In the procedure of AlN formation, through the carbothermal reduction of Al_2O_3 in a flowing N_2 atmosphere, the carbothermal nitridation mechanism may include intermediate gas phase reactions and solid-state reaction at temperatures above 1500 °C [11, 12]. As the temperature increasing, the Al_2O_3 will dissociate into Al_2O or Al vapor, which may be reduced by carbon or CO and subsequently nitrided to yield AlN. In this case, the solid-gas reaction mechanism played a determining role in the kinetics of carbothermal reduction. But at relatively low synthetic temperature, e.g. 1600 °C, the Al_2O_3 dissociation became difficult, so the AlN formation was conducted by solid phase reaction. In this course, the rate of reaction was controlled by gas phase diffusion, so the products maintain the morphologies of the raw materials. In this study, the synthesis of AlN fibres was undergone at temperature 1650 °C in flowing nitrogen atmosphere. At this temperature the fibres with sillimanite phase will dissociate into mullite ($3Al_2O_3{\cdot}2SiO_2$) SiO_2 and some liquid phase, but in this case, the Al_2O_3 and SiO_2 will be reduced by carbon in flowing nitrogen atmosphere to yield AlN, SiC or Si_3N_4. However, before the formation of SiC or Si_3N_4, SiO_2 will dissociate into SiO and O_2, subsequently reduced by carbon to yield SiC or nitrided by flowing N_2 to yield Si_3N_4. The SiC or Si_3N_4 were transferred to the outside of the furnace with flowing nitrogen, so the SiC or Si_3N_4 could not be discovered in synthesized products. But if the heating time decreases, they do not transfer to the outside of the furnace fully, so the SiC or Si_3N_4 will exist in products. In order to determine this proposal, a sample was made by short time, XRD patterns confirmed that there was SiC in this sample (Fig. 3), but the Si_3N_4 weren't found. Al_2O_3 in the raw materials will be reduced by carbon and subsequently nitrided to yield AlN, and in this course, the subsequent reaction was by gas-phase diffusion, the main reaction of carbothermal reduction was solid-phase reaction mechanism. So after the reaction the products maintained the morphologies of raw materials fibres to yield AlN fibres. According to above analysis, a model of AlN fibres *in-situ* synthesized by carbothermal reduction of aluminum silicate has been developed (Fig. 4).

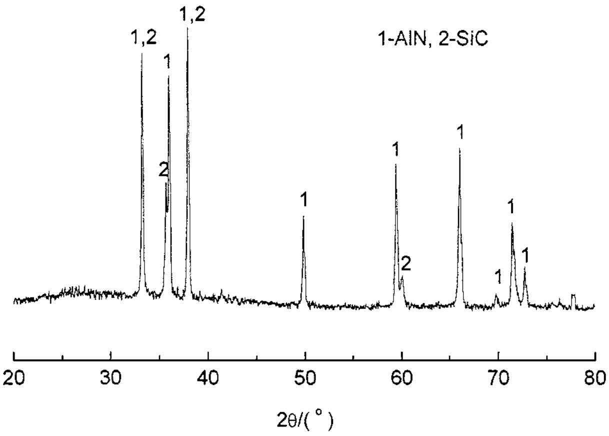

Figure 3 The X-ray pattern of AlN with SiC.

4. Conclusions

1. AlN fibres were successfully *in-situ* synthesized by aluminum silicate fibres carbothermal reduction.

2. In the process of AlN fibres synthesis, the aluminum silicate fibres was carbothermally reduced by solid-phase reaction which was controlled by the gas phase diffusion, subsequently nitrided to yield AlN

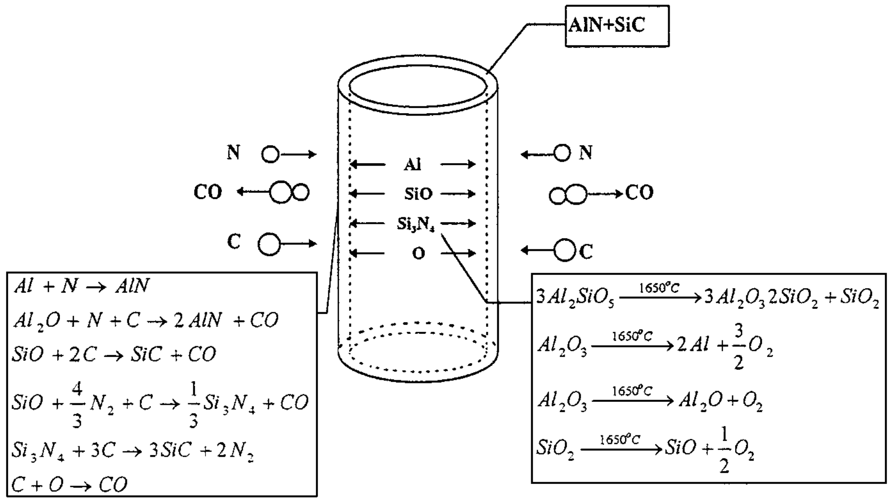

Figure 4 A model of the carmothermal nitriding of aluminum silicate fibres.

fibres. So the products remained the morphologies of raw materials fibres.

3. The AlN fibres were polycrystal fibres composited with small grains, and as the heating time increasing the grains will grow larger.

4. Before Al_2O_3 was reduced by carbon, the SiO_2 in aluminum silicate fibres was first dissociated into SiO and O_2, subsequently, SiO will react with carbon to yield SiC, which are transferred to the outside of the furnace with the flowing nitrogen, so the SiC didn't exist in synthesized products.

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