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Synthesis of $MgSiN_2$ Cuboids by a Solid-state Reaction

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$MgSiN_2$ cuboids were prepared using Si, Mg, and NaN_3 powders as reactants in autoclaves at 350–500 °C for 12 h. SEM, TEM, and HRTEM images reveal that the product is composed of crystalline $MgSiN_2$ cuboids. The synthesis parameters such as the ratio of the reactants, temperature, and reaction time were investigated. It is found that using appropriate excess of Mg and NaN_3 favors the formation of $MgSiN_2$.

Magnesium silicon nitride ($MgSiN_2$) has attracted great interest due to its high fracture toughness, fracture strength, hardness, good oxidation resistance, high thermal conductivity, and high electrical resistive.[1] These properties have made it a potential candidate as substrate material for high-density integrated circuit packaging.[2] $MgSiN_2$ also can be used as an effective additive in fabrication ceramics due to its high thermal conductivity.[3]

In the past the decades, various methods have been applied to synthesize $MgSiN_2$ powder, such as carbothermal reduction of magnesium metasilicate at 1400 °C under nitrogen atmosphere,[4] solid-state metathesis using Mg_3N_2 and SiO_2 at different flame temperatures above 1100 °C,[5] direct nitridation of $Si/Mg_2Si/Mg/Si_3N_4$ powder mixture at 1350 °C,[6] Mg_2Si at 1600 °C,[7] or mixtures of Mg_3N_2/Si_3N_4, Mg/Si_3N_4, or Mg/Si in the temperature range of 800–1500 °C.[8]

Recently, a lot of effort has been made to prepare $MgSiN_2$ via energy efficient methods or at lower temperatures, for example, combustion synthesis by direct nitridation of different powder mixtures.[9] It was reported that $MgSiN_2$ powders were synthesized through the reaction of Mg, $SiCl_4$, and $N_2H_4{\cdot}HCl$ in autoclaves at 450 °C.[10] As silicon powder is less toxic than $SiCl_4$ and widely used as the raw material to prepare Si_3N_4 powders in industry, herein we present the preparation of $MgSiN_2$ via the solid-state reaction of Mg, Si powder, and NaN_3 at 350–500 °C in an autoclave.

In a typical experimental procedure, 30 mmol of Mg powder (100–200 mesh), 20 mmol of Si powder (200 mesh), and 5 mmol of NaN_3 were mixed and placed into a 20-mL stainless-steel autoclave in ambient atmosphere without inert gas protection. The autoclave was sealed, then heated from room temperature to 350–500 °C at a rate of 10 °C min^{-1}, and maintained at 350–500 °C for 12 h in a furnace. After the autoclave was cooled to room temperature naturally, the raw products were washed with anhydrous ethanol, dilute hydrochloric acid, and distilled water, and finally dried in a vacuum oven at 60 °C for 24 h.

The final product was characterized by X-ray powder diffraction (XRD, Bruker D8 with Cu Kα radiation), field emission scanning electron microscopy (FE-SEM, JSM-6700F) equipped with energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM, Hitachi 7000), and High-resolution TEM (HRTEM, JEOL 2100). Thermal gravimetric analysis (TGA) was taken on an SDT Q600 V8.0 Build 95 thermal analyzer.

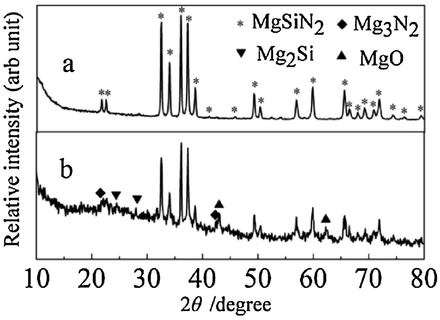

Figure 1. XRD patterns of the products obtained after (a) and before (b) the acid treatment ($MgSiN_2$ marked with $*$, Mg_3N_2 marked with ◆, Mg_2Si marked with ▼, and MgO marked with ▲).

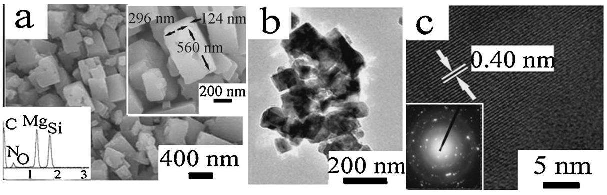

Figure 2. (a) Typical FE-SEM images (inset: EDX analysis), (b) a typical TEM image, (c) HRTEM image of a part of $MgSiN_2$ cuboid (inset: SAED pattern).

A typical XRD pattern prepared at 500 °C for 12 h is shown in Figure 1a. The diffraction peaks can be indexed as orthorhombic $MgSiN_2$. The calculated cell parameters, $a = 5.260$ Å, $b = 6.463$ Å, and $c = 4.951$ Å, are in good agreement with the reported values (JCPDS Card No. 52-0797). The strong and sharp diffraction peaks show that the as-prepared products are well. Figure 1b is the XRD pattern of the raw product. It is found that the raw product before acid treatment contains MgO, the oxygen element perhaps comes from air in the autoclave.

The morphology and structure of the products were examined by TEM, FE-SEM, and HRTEM. The SEM image (Figure 2a) indicates that the product is mainly composed of $MgSiN_2$ cuboids. The magnified SEM image (right-upper corner) further reveals that cuboids have lengths in the range of 300–600 nm, widths of 100–300 nm, and height of 100–200 nm. Figure 2b shows the TEM image of the as-synthesized sample. It can be observed that the product is composed of nanoparticles and a large number of cuboids. HRTEM image (Figure 2c) shows that the interplanar distance of the product is 0.40 nm, which is consistent with the *d* spacing of (110) planes of $MgSiN_2$ (JCPDS card No. 52-0797). The left-bottom corner inset in Figure 2c shows the typical SAED pattern of a cuboid, indicating the polycrystalline nature of the cuboid. The typical EDX spectrum (left-bottom corner inset in Figure 2a) of the $MgSiN_2$ cuboids reveals the presence of Si, Mg, N, and O (C

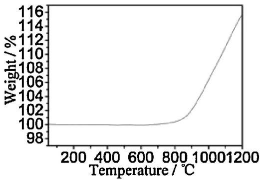

Figure 3. TGA analysis of the sample carried out in air at a heating rate of 20 °C min^{-1}.

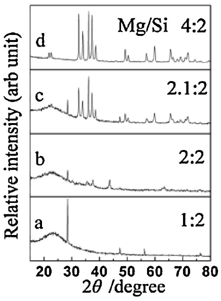

Figure 4. The XRD patterns of $MgSiN_2$ prepared from different Mg/Si ratios: (a) 1:2, (b) 2:2, (c) 2.1:2, and (d) 4:2.

signal originates from the SEM grid). Quantification of the spectrum gives the O components (atom %) of ca. 2%. Figure 3 shows the typical TGA curve of the sample. It is obvious that $MgSiN_2$ powders are oxidation-resistant in air up to 820 °C, which is in good agreement with the reported values.[2]

The ratio of Mg/Si was a key factor for the formation of $MgSiN_2$. If inadequate Mg is used, the diffraction peaks of Si are observed in Figure 4a, but no $MgSiN_2$ can be detected. When stoichiometric Mg was used, with the Mg/Si of 2:2, product contained Si and low crystallinity $MgSiN_2$ was produced (Figure 4b). When a bit excess Mg was used (Mg/Si ratio = 2.1:2), crystalline $MgSiN_2$ (Figure 4c) was obtained, but the Si peak in the XRD pattern was still obvious. Increasing the molar ratio of Mg/Si to 3:2, $MgSiN_2$ with high crystallinity can be obtained (Figure 1a). Varying the molar ratio of Mg/Si between 4:2 (Figure 4d) to 8:2 did not significantly influence the crystallinity of $MgSiN_2$, so the optimal Mg/Si ratio used was 3:2. The experimental results indicated that excess Mg favors the formation of $MgSiN_2$.

The experimental parameters such as reaction temperature, time, and reactants were investigated to determine the reaction mechanism. No $MgSiN_2$ was obtained when the temperature was set below 300 °C, while $MgSiN_2$ products with good crystallinity were obtained at 350–500 °C. The diffraction peaks of silicon were frequently found coexisted with those of $MgSiN_2$ in the XRD patterns if the reaction time was shorter than 3 h. The prolonged reaction time (6–12 h) did not significantly influence the final morphology of the product. Though stoichiometric ratio (13.3 mmol) of NaN_3 can generate crystalline $MgSiN_2$, unreacted silicon was always detected in the mean time. When excess NaN_3 (54 mmol) was used, pure $MgSiN_2$ can be obtained. Excess NaN_3 used in our experiment resulted in a high pressure (ca. 26 MPa estimated according to the ideal gas law) in the autoclave at 500 °C, which is an important factor for the formation of crystalline $MgSiN_2$ powders at low temperature, its role is similar to the synthesis of silicon nitride.[11] Besides, the newly formed N_3 (originates from the decomposition of NaN_3) possesses high reactivity, which is favorable for the formation of $MgSiN_2$. When silicon powder was replaced by SiO_2 or diatomite, $MgSiN_2$ was also obtained.

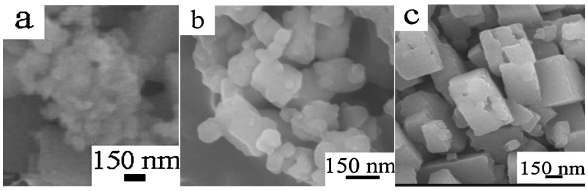

Figure 5. The SEM images of $MgSiN_2$ nanocrystals obtained with different heating time: (a) 3, (b) 7, and (c) 12 h.

It is found that different heating time plays important roles on the final formation of regular shaped products (Figure 5). The shape evolution and growth of $MgSiN_2$ crystals from irregular particles (about 70 nm, Figure 5a) to irregular blocks (about 200 nm, Figure 5b), and to cuboids (about 500 nm, Figure 5c) occurred with the prolonged reaction time. And these $MgSiN_2$ cuboids were composed of aggregate of small particles.[10]

The overall reaction probably can be described as follows:

$$2Si + 3Mg + 5NaN_3 \rightarrow 2MgSiN_2 + 5Na + 31/6N_2 + 1/3Mg_3N_2 \tag{1}$$

In summary, single-phase $MgSiN_2$ powders were synthesized by a solid-state reaction of Si, Mg, and NaN_3 powder in an autoclave at 350–500 °C for 12 h. The average yield of the products is about 90% according to the amount of Si. The effects of synthesis parameters such as the ratios of the precursors, reaction temperature, and different silicon sources on the final formation of $MgSiN_2$ powder were investigated. It is found that appropriate excess of Mg and NaN_3 favors the formation of $MgSiN_2$.

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