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Short Communication

Catalyst-assisted synthesis of α-Si_3N_4 in molten salt

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Abstract

Silicon nitride (Si_3N_4) powder was synthesised under a nitrogen gas flow (150 mL/min) using molten salt media at relatively low temperatures (950–1350 °C) to investigate the effects of temperature and cobalt (Co) content on its phase assembly and micro-morphology. Analysis of purified α-Si_3N_4 obtained using X-ray diffraction, scanning electron microscopy, transmission electron microscopy and energy-dispersive X-ray spectroscopy revealed that the fabrication of α-Si_3N_4 from silicon by molten salt media is possible at temperatures as low as 1050 °C. Furthermore, Co played an important role in accelerating Si nitridation through the formation of a Co–Si liquid phase, with overall conversion increasing from 5% to 60% with the addition of 0.5 wt% Co at 1150 °C. At temperatures below 1350 °C, silicon nitride exists mainly as flaky nanoparticles, but at higher temperatures changes to α-Si_3N_4 nanorods that are 200–500 nm in diameter and 500–1000 nm in length. The growth of these nanorods and nanoparticles was governed by the vapour–liquid–solid and vapour–solid mechanisms.

Keywords: B. Microstructure-final; D. Si_3N_4; Cobalt catalyst; Molten salt

1. Introduction

Silicon nitride (Si_3N_4) is a promising engineering material, as it offers excellent mechanical properties in combination with good refractoriness, thermal shock resistance, chemical stability, creep resistance, and wear resistance even at high temperatures [1–4]. This has led to its widespread use in electronics, optics, machinery, advanced engineering applications, and metallurgical industries [5–7], with it being fabricated by chemical vapour deposition (CVD) [8], sol–gel synthesis [9,10], direct nitridation of silicon [11], carbothermal reduction nitridation [12,13], combustion synthesis [14,15], or SiO vapour ammonolysis [16]. However, each of these techniques presents its unique disadvantages. For example, the CVD and sol–gel methods are complex, expensive, and environmentally unfriendly, while the other techniques tend to introduce impurities into the final product. Therefore, there is still a need to develop a more convenient, economical, and effective method for producing Si_3N_4 powder.

Molten salt synthesis (MSS) is a well-established low-temperature technique that has attracted increasing interest in recent years, as its reliance on the use of water-soluble salts with low melting points (e.g., alkali chlorides and sulphates) results in very low levels of impurities in the final product. As such, it has been used to produce a variety of ceramic powders with whisker, nanowire, or hollow sphere morphologies [17–21]. The introduction of nitrogen gas to the reaction system, known as molten salt nitridation synthesis (MSNS), has also made it possible to form titanium nitride whiskers on graphite flakes [22]. This study therefore looks at whether MSNS can be adapted to the preparation of Si_3N_4 powder in NaCl–NaF media catalysed by Co. The effects of the Co content on the phase composition, microstructure, and growth mechanism of powders sintered at different temperatures, are herein discussed to provide insight into the potential for this process to be applied to other nitrides.

2. Experimental materials and procedure

Powders of Si (purity ≥ 99% w/w, particle size ≤ 10 μm), Co (purity ≥ 99% w/w, particle size ≤ 2 μm), NaF (purity ≥ 99% w/w), and NaCl (purity ≥ 99% w/w) were used as

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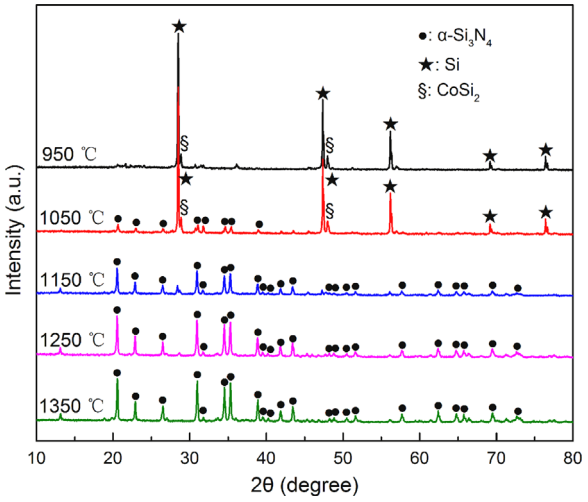

Fig. 1. XRD patterns of samples obtained after heating for 5 h at different temperatures.

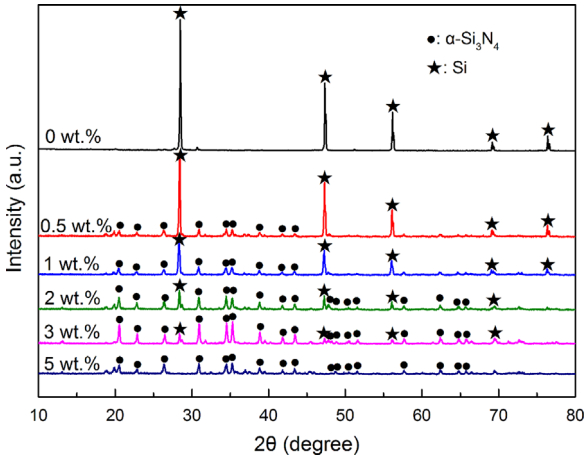

Fig. 2. XRD patterns of samples containing various amounts of Co after 5 h nitridation at 1150 °C.

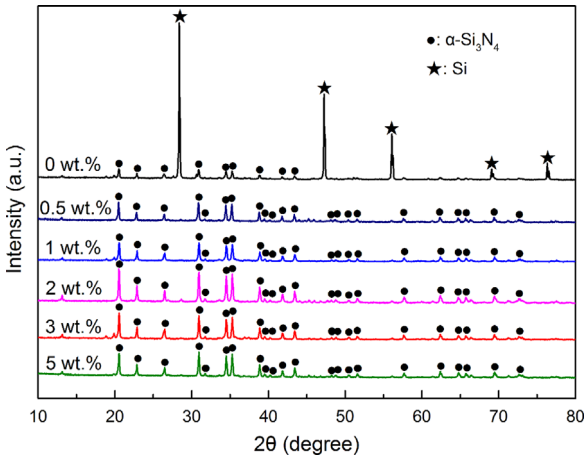

Fig. 3. XRD patterns of samples containing various amounts of Co after 5 h nitridation at 1250 °C.

the raw materials. These were mixed to give a Si-to-salt molar ratio of 1:3, with the NaCl-to-NaF weight ratio being fixed at 2:1. The amount of Co addition was varied to produce concentrations of 0, 0.5, 1, 2, 3, and 5 wt% Co. Once mixed, each powder was placed in an alumina crucible and was heated to 950–1350 °C for 5 h under a high-purity (≥ 99.999%) N_2 gas atmosphere. After cooling to room temperature, the solidified mass was repeatedly washed with hot distilled water and was filtered several times to remove any residual salt.

The phase morphology of the nitrided powders was analysed by X-ray diffraction (XRD, Philips, X'Pert Pro), while the microstructure was observed by scanning electron microscopy (SEM, FEI, Nova 400 Nano) and a high-resolution transmission electron microscope (HRTEM, JEOL, JEM-2000F) capable of energy dispersive X-ray spectroscopy (EDS). To calculate the overall conversion of the Si powders, ARL 9900 Series X-ray workstation (XRF) (combined with XRD) was performed by Thermo Scientific.

3. Results and discussion

The effect of temperature on the synthesis of α-Si_3N_4 (JCPDS card no. 01-076-1408) is presented in Fig. 1; and as can be seen, the α-Si_3N_4 peaks first begin to appear at 1050 °C and then continue to increase in height with temperature. Thus, at temperatures between 950 °C and 1050 °C, the powder produced is essentially composed of α-Si_3N_4 and Si (JCPDS card no. 01-077-2109) with a small amount of $CoSi_2$ (JCPDS card no. 01-074-1371). However, when the temperature is increased to 1250 °C, the Si peaks disappear and a single α-Si_3N_4 phase is obtained. Therefore, it can be said that the amount of α-Si_3N_4 increases with the temperature in the heat treatment.

The XRD patterns in Fig. 2 were obtained from samples containing 0–5% Co after 5 h of nitriding at 1150 °C. As the figure shows, the α-Si_3N_4 and a trace amount of Si was present in the reference sample; however, the intensity of the α-Si_3N_4 peak reaches a maximum at the Co content of 3 wt%. This peak remains stable when the Co content is increased further to 5 wt%, but notably, the Si diffraction peak disappears. The XRD patterns in Fig. 3 indicate that increasing the nitriding temperature to 1250 °C significantly alters the effect that the Co content has, with only 0.5 wt% Co being needed for the Si peak to disappear. This means that a higher temperature makes Co a far more effective catalyst for the nitridation of Si powder.

The XRD patterns in Figs. 1–3 were used to calculate the relative proportion of α-Si_3N_4 produced, with Fig. 4 showing the effects of heat treatment temperature and Co content on the overall conversion of Si. Tables 1 and 2 show the overall conversion of Silicon powder under different conditions. It is evident in Fig. 4(a) that the relative content of α-Si_3N_4 gradually increases with calcining temperature up to 100% at 1350 °C, while Fig. 4(b) shows that the formation of α-Si_3N_4 increases linearly with an increase in the Co content. Note that there is very little nitridation of the Si powder at 1150 °C in the absence of Co, but that this increases quite dramatically with the addition of Co. For instance, adding just 0.5 wt% Co results in 60% nitridation of the Si powder, while an addition of 5 wt% results in almost complete nitridation. Similarly, although 40% nitridation was achieved at 1250 °C without Co,