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Synthesis of Si_3N_4 powder by powder metallurgy method in atmospheric pressure N_2: A review

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***Keywords*— Si_3N_4, direct nitridation, metals catalyst.**

***Abstract*—** *Catalytic effects of metals, which are often involved in the fabrication of silicon nitride product, on the direct nitridation of silicon have been reviewed through this study. A nitridation echancement effect has also been observed with the addition of some metals. The metals are mixed with Si in separate mass ratios before reaction. The results showed that the conversion from Si to Si_3N_4 increased markedly with increasing content of the catalyst. From there, it helps to reduce the reaction temperature as well as energy costs for the direct nitridation process. Besides, metal catalysts also react with Si to create Me_xSi_y compounds that reduce the high-temperature resistant properties of Si_3N_4. Therefore, it is necessary to choose appropriate catalysts so that the product retains its preeminent properties.*

I. INTRODUCTION

Silicon nitride (Si_3N_4) is one of the most promising structural materials for high-temperature and high mechanical-stress applications because of its excellent properties such as high strength retention at elevated temperature, good thermal shock resistance, high-temperature deformation resistance as well as high corrosion resistance [1-12]. Thus, Si_3N_4-based materials are extensively used in a variety of areas such as in chemical reaction vessels, heat exchanger bearings, engine and gas turbines, high-temperature components, automotive parts and aerospace vehicles [13-15]. Si_3N_4 exists in two main configurations: the α-Si_3N_4 begins to form at 1400ºC and turns into β-Si_3N_4 at temperatures above 1600ºC. There is also a very rare γ-Si_3N_4, but this configuration is formed at very high pressure and temperature[1] and hence beyond the scope of this investigation.

As far as concerned, there are three main methods and several unpopular methods used for the production ofSi_3N_4 powders [17-23]:

- *Carbothermal reduction method*

The carbothermal reduction of SiO_2 powder under nitrogen was the earliest used method for Si_3N_4 production.

$$3SiO_2 + 6C + 2N_2 = Si_3N_4 + 6CO \quad (1)$$

- *Direct nitridation method*

The Si_3N_4 powder can be prepared by heating powdered silicon up to between 1300ºC and 1400ºC in nitrogen atmosphere.

$$3Si + 2N_2 = Si_3N_4 \quad (2)$$

During the reaction, the silicon sample weight increases progressively due to the chemical combination of silicon and nitrogen.

- *Silicon amide method*

The development of the long-known but little-used silicon amide route relies on the increasing availability of

low-cost silicon tetrachloride ($SiCl_4$). The decomposition of silicon diimide ($Si(NH)_2$) results in amorphous Si_3N_4, which is converted to the **α**-Si_3N_4 by heating up to 1400°C–1500°C under nitrogen.

$$SiCl_4 + 6NH_3 = Si(NH)_2 + 4NH_4Cl \quad (3)$$

$$3Si(NH)_2 = Si_3N_4 + N_2 + 3H_2 \quad (4)$$

➢ *Other methods*

Several alternative production methods of Si_3N_4have been presented; however, they have not been used widely for various technological or economic reasons, such as high cost, slow reaction kinetics or the development of undesirable particle morphologies. Some of the listed as below:

- $3SiS_2 + 4NH_3 = Si_3N_4 + 6H_2S$ (5)
- $3SiC + 4NH_3 = Si_3N_4 + 3CH_4$ (6)
- $3SiO_2 + 4NH_3 = Si_3N_4 + 6H_2O$ (7)

The direct nitridation of Si powder is regarded as a low-cost and straightforward route for the large-scale production of Si_3N_4 powder and bulk Si_3N_4 based materials[2], but the high nitridation temperature and long reaction time are the major problems of the method that need to be solved.

One of the strategies considered to solve this problem is to use a suitable catalyst for the nitridationprocess of Si. Several investigations have shown positive effects of metals on the processsuch as on removing the silica layer[1] or the formation of Me_xSi_y which promotes the nitridation process[2].Recently, many reports have been used a catalyst toapply the nitridation of Si at lower temperatures [1,13,24-30]. Fe is the most popular catalyst for enhancing the nitridation of silicon and is generally an impurity in low-purity silicon powder[3]. The catalytic effects of other metals, such as Fe,Cr, and Co on the nitridation of silicon have also been investigated [13,24-27].

II. THE EFFECT OF METALS CATALYSTS

1. *Iron metal (Fe)*

Iron as a transition metal will have positive effects on removing the silica layerand aid the overall nitridation process by forming a liquid phase composition of $FeSi_2$ attemperatures exceeding 1212°C[4].

Figure 1 shows the effect of Fe catalyst on the nitridation of Si. It can be seen that only a small amount of Fe (1000 ppm) has promoted the process significantly (from 30% without Fe to ~38% with 1000 ppm Fe). When Fe content increases to over 1000 ppm, mainly β-Si_3N_4 phase was formed.

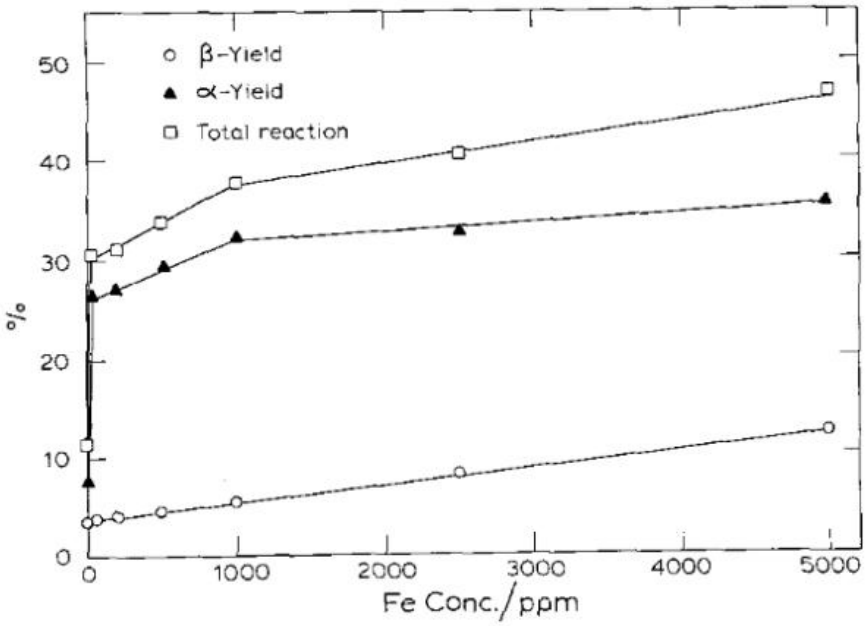

Fig1: Effects of Iron content on the overall conversion of silicon at 1350oC for 10h[1]

2. *Chromium metal (Cr)*

Chromium is considered asa typical candidate to promote direct nitridation. Because chromium, chromium nitride, and Cr_xSi_y phases all have high melting points and good high-temperature properties, their remaining after the nitridation will not have significant negative effects on high-temperature properties of the final product materials.

The study of Feng Liang et al [2] showed the positive expression of the metal catalyst Cr. Figure 2 displayed the relationship between Cr content and the overrall conversion of Si with different temperature.

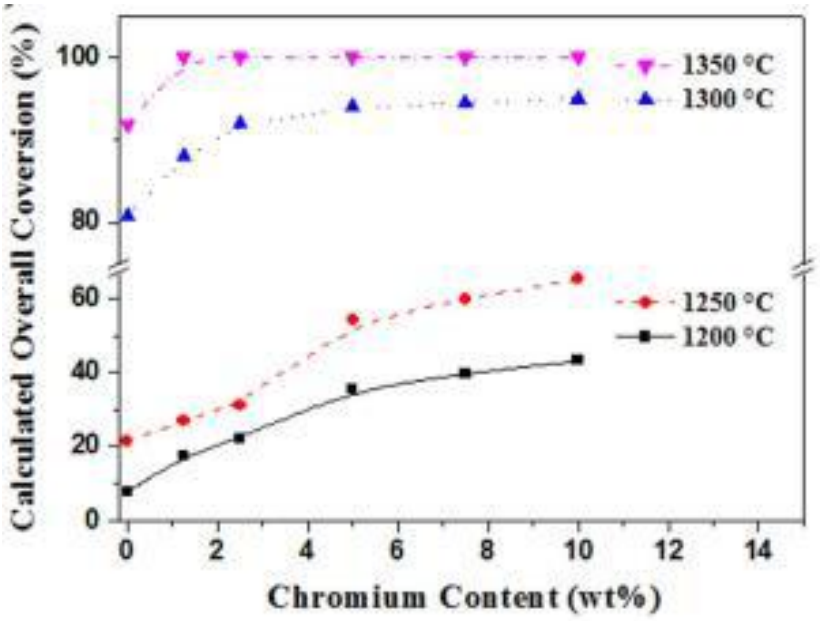

Fig.2: Effect of Cr content on the overall conversion of Si in samples resultant from 3h nitridation at different temperature[2]

As can be seen, the addition of chromium affected the nitridation process significantly. At 1200ºC and 1250ºC, the overall conversion (OC) of Si to Si_3N_4 in the reference samples without Cr was low. However, it increased evidently with the increasing Cr content. For example, at 1250ºC, the OC was only ~21% in the case of no Cr addition but increased significantly to ~66% in the sample containing 10 wt% Cr. At higher temperatures such as 1300ºC and 1350ºC, the effect of the catalyst reaches the conversion rate limit even with low added Cr content (~94% with 5 wt% Cr at 1300ºC and ~100% with 1,25% wt% Cr at 1350ºC). Overall, Cr catalyst reduces the nitridation process temperature of Si and the product still reaches a high ratio Si_3N_4.

Figure 3 presentsthe XRD patterns of samples containing 0-10% Cr after 3h nitridation at 1250 ºC and 1350 ºC respectively. At 1250 ºC, unreacted Si peaks remained as the main phase in the sample without catalyst. With increasing Cr content, the α/β Si_3N_4 peaks appearednoticeably and Cr_2N was detected in the sample containing 10 wt% Cr. At 1350ºC, α- and β-Si_3N_4 were identified in the reference sample, along with some unreacted Si. On the other hand, in thesample containing 1.25 wt% Cr, Si disappeared and only **α**- and **β**-Si3N4 phases were present. With more than 5 wt.% of chromium, **α**- and **β**-Si_3N_4 remained as the primary phases;however, minor Cr_2N and two other impurity phases (appeared to be Cr_3Si and Cr_5Si_3) were detected.

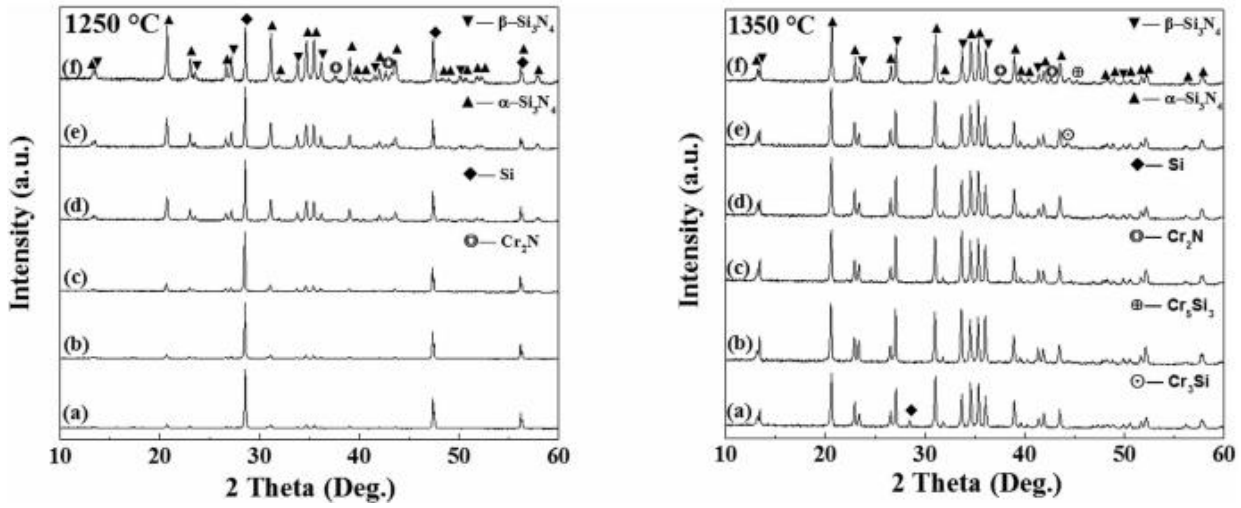

Fig.3: XRD patterns of samples containing various amounts of Cr: (a) 0, (b) 1.25, (c) 2.5, (d) 5, (e) 7.5, and (f) 10 wt%, after 3h nitridation at 1250ºC and 1350ºC, respectively[2]

3. *Cobalt metal (Co)*

According to the study of Juntong Huang et al[5], the nitridation process of Si is driven by metal Co. The effect of Co on the direct nitridation of Si is displayed in Figure 4.

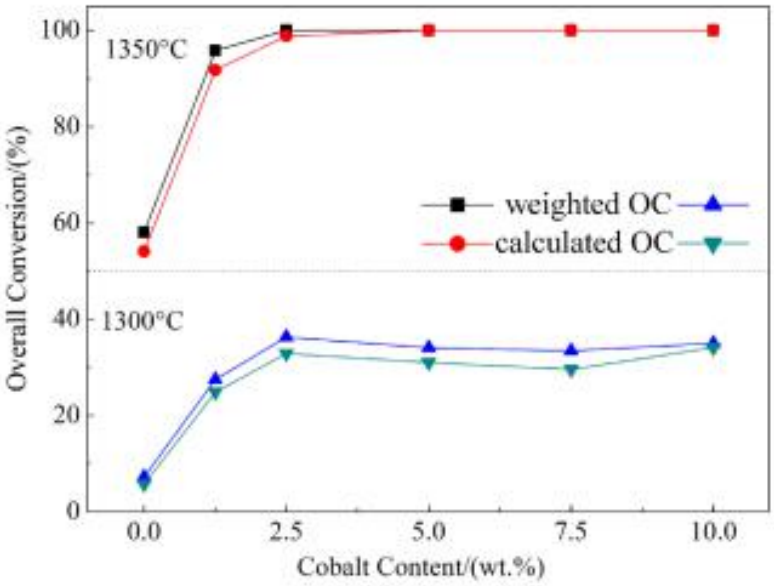

Fig.4: Effects of cobalt content on the overall conversion of silicon at different nitriding temperatures for 3h[5]

At 1300 ºC, the nitridation extent (OC) in thereference sample without Co was very low (only 7%).However, it increased evidently to maximally 38% in theCo catalyzed samples. Upon increasing the temperature to 1350 ºC, the OC in the reference sample increased to 54%, whereas a much greater OC was achieved in a Co-catalyzed sample. For example, with the addition of 1.25% Co, >90% OC was achieved, and with the addition of 2.5% Co, nearly all of the Si had been converted. The above results indicated that Co exhibited a strong accelerating effect on the conversion from Si to Si_3N_4.

Shown in Figure 5 are XRD patterns of the samples containing 0-10% Co after 3h nitridation at 1350 ºC.

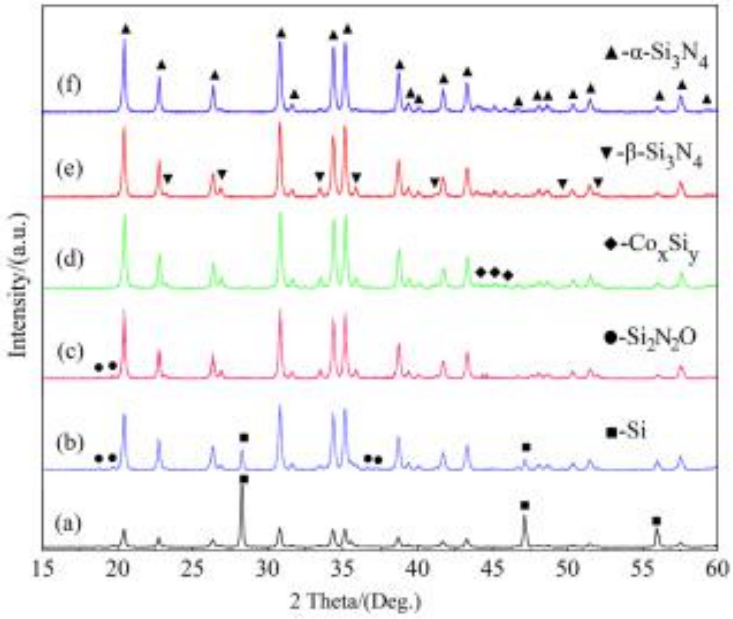

Fig.5: XRD patterns of the samples containing various amounts of cobalt after 3h nitridation at 1350ºC: (a) 0, (b) 1.25, (c) 2.5, (d) 5.0, (e) 7.5 and (f) 10%[5]

Without Co, the peaks of Si appear very clearly. When Co increased to 1.25%, the intensity of α-Si_3N_4 peaks increased evidently while the intensity of the Si peaks decreased. On increasing Co to 2.5%, the Si diffraction peaks disappeared, and only α-Si_3N_4 along with a small amount of β-Si_3N_4were identified, indicating a complete conversion from Si to Si_3N_4. On further increasing of Co to ≥ 5%, there were no obvious changes in the primary phases but minor amounts of impurity phase (presumably Co_xSi_y) were detected.

4. *Copper metal (Cu)*

Like the above metals, Cu also has positive effects on the nitridation of Si.

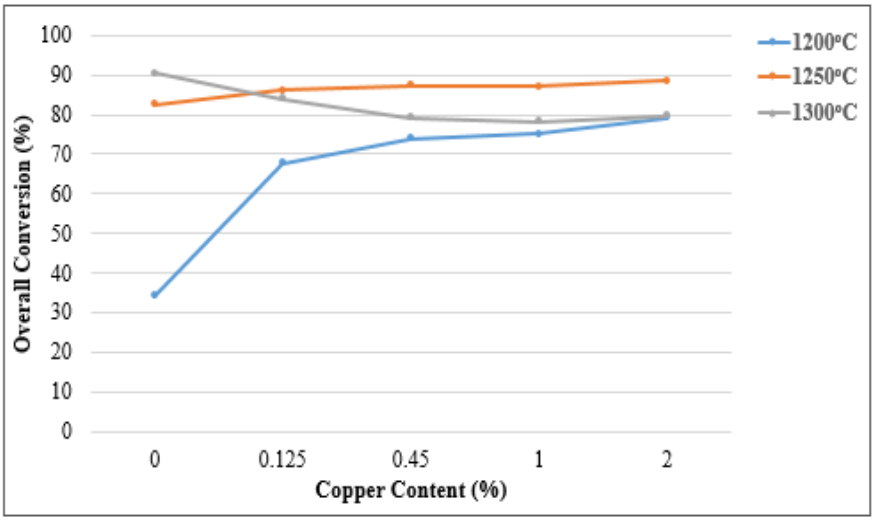

Fig.6: Effects of copper content on the overall conversion of silicon at different nitriding temperatures for 3h[6]

As shown in Figure 6, the nitridation of Si with 0.125% Cu at 1200°C yields an overall conversion as high as almost double that from bare Si. The overall conversion at 1200°C also increases with the Cu content and approaches the conversion level achieved in the nitridation of bare Si at 1250°C. But when the temperature is increased to 1250°C, the effects of Cu on the nitridation of Si are also unclear. It even decreased when raised to 1350°C.

5. *Calcium metal (Ca)*

Ca is the metal, among all the metals investigated, that enhances only the formation of α-Si_3N_4. Purified α-Si_3N_4 can be obtained with only a small amount of Ca (0.125%) added.

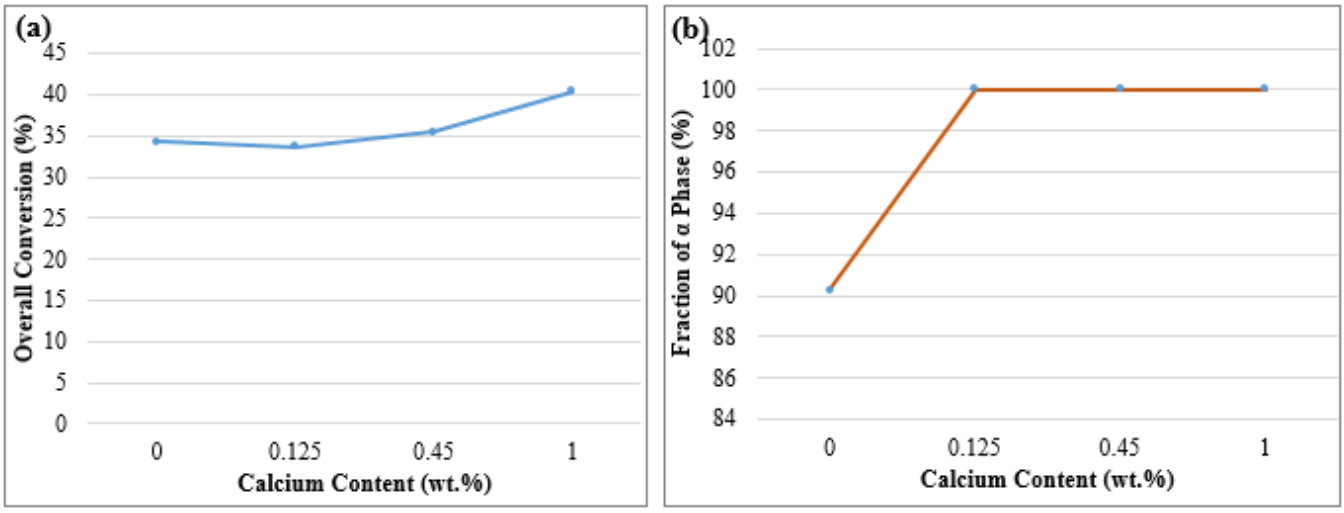

Fig.7: Effects of calcium content on the (a) overall conversion and (b) formation of α-phase after 3h nitridation at 1200°C[6]

III. CONCLUSIONS

Metal catalysts have a positive effect on the nitridation of Si as the content of the catalyst increases, the nitridation process is accelerated. The used metal catalysts was an attractive method to reduce the reaction temperature and due to its high functionalization and high efficiencyfor realizing energy consumption saving. However, it should be noted when selecting the metal catalysts and the content in a reasonable manner as the nitridation process will create Me_xSi_y compound that can reduce the high-temperature resistant properties of Si_3N_4.Future studies on Si_3N_4 ceramics should focus on adding attractive properties, such as high thermal conductivity and high wear resistance, while maintaining good mechanical properties.

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