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Phase Analysis and Study of the Microstructure of Cordierite-Si_3N_4 Composite Synthesis by Nano- and Micro-Sized Silicon Particles

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In this study the effect of in situ Si_3N_4 formation on the microstructure changes of cordierite-Si_3N_4 composite prepared using nano silicon powders, which obtained in a high energy planetary ball mill, and micro silicon powder was investigated. Different mixtures of the cordierite with nano and micro silicon powders were prepared and sintered in a tube furnace at different temperatures in a nitrogen atmosphere. Microstructural characteristics, thermal properties and phase analysis of these composites were carried out by using scanning electron microscopy (SEM), simultaneous thermal analysis (STA) and X-ray diffraction analysis (XRD). It was found that micro and nano silicon particles have different reaction characterizations with the nitrogen in the matrix of cordierite at various temperatures. Results showed that by using nano silicon powder the formation of silicon nitride bonding will be increased which could be related to the acceleration of nitride phase at temperatures lower than the temperature of liquid phase formation.

Keywords Cordierite; microstructure; nano and micron silicon powder; silicon nitride

Introduction

Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) is a technically important ceramic with a low thermal expansion coefficient, a low dielectric constant and high chemical and mechanical stability [1–4].These characteristics make it an interesting candidate for many industrial applications such as refractories, heating elements, thermal and electrical insulations, filters, honeycomb catalyst, membranes and diesel engines applications [5–6]. However, cordierite ceramics have a relatively narrow firing range temperature, low mechanical strength and thermal conductivity, thus it exhibits shorter service life under thermal fatigue. The main disadvantages of cordierite composite are related to the type of bonding of cordierite composite [7–8].

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Silicon nitride, because of good thermo-mechanical properties is one of the most promising materials [9–10] that could be used as an effective bonding in ceramic materials. Also Si_3N_4 shows good thermal stress resistance due to the low coefficient of thermal expansion, relatively good resistance to oxidation compared to other high-temperature structural materials and suitable strength to weight ratio for design of engineering components in ceramic industries [11–13].

Pasto et al. [14] have been developing efforts on Si_3N_4-cordierite composite ceramics which are being tailored for diesel engine applications. They discovered that the thermal conductivity of these ceramics is lower than that of current sintered silicon nitride (SSN), and much lower than that of silicon carbide. They also found that this composite represents a low thermal expansion coefficient and small reduction in strength and toughness compared to SSN [14].

The present work aims to fabricate the in situ Si_3N_4 in the matrix of cordierite using nano and micro silicon powders in a nitrogen atmosphere by using the reaction bonding process at relatively low temperatures. The effect of silicon nitridation variables including particle size of silicon powder and the reaction temperature were investigated. Result showed that by using nano silicon powder the formation of silicon nitride bonding will be increased which could be related to acceleration of Si_3N_4 formation. Because of nitride phase formed before liquid phase formation during firing of cordierite. On the other hand, without using additives and firing at a temperature lower than liquid phase formation, bodies with high amount of porosity and a high thermal shock resistance could be obtained.

Experimental Procedure

British kaolin (Z. lids), Iranian talc (Jandagh) and $Al(OH)_3$ (Nabalox) were used as raw materials for cordierite synthesis. The Silicon powder used was produced by Elkem Company with 98.5% purity. The chemical composition of raw materials used in this research is shown in Table 1.

The raw materials for making cordierite were prepared according to the MgO-SiO_2-Al_2O_3 phase diagram. To prepare cordierite composite, powders were ball-milled in a 500 ml porcelain jars for 24 h with alumina balls to obtain homogeneous slurries. After drying at 80°C for 24 h and sieving through a 32-mesh screen, the mixed powders were uniaxially pressed into the discs-shaped specimens with thickness and diameter of 5 mm and 25 mm respectively, under 50 MPa pressure. The specimens were sintered in the air at 1200°C to 1400°C for 3 h soaking time with a heating rate of 5°C/min. The bulk density of the sintered products was determined by Archimedes method in order to select the best sintering temperature of cordierite.

Nano-sized silicon powder was prepared by a high energy planetary ball mill, using polymer cylinder and zirconia balls in two sizes (Q = 10, 20 mm) for 200 h in an Ar

Table 1. Chemical composition of raw materials

Raw materials	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	K_2O	Na_2O	L.O.I
Kaolin (Z.lids)	47.1	36.7	0.85	0.17	0.25	0.36	1.02	0.03	13.25
Talc (Gndagh)	57.5	25	0.5	0.08	31.5	0.85	0.46	0.12	7
Alumina (Nabalox)	0.02	99.6	0.03	—	—	—	—	—	3.45

atmosphere. The ratio of the mass of the milling media bodies to the mass of the powder was considered 20:10. The particle size of milled silicon powder was measured by a laser particle size analyzer (Malvern-U.K-Model of ZN 3200).

In order to synthesis cordierite-Si_3N_4 composite, the best cordierite sample, i.e. the sample with higher density fired at different temperatures was selected. These samples were crashed and sieved through a 72-mesh size and then mixed with 1, 3, 5 and 10 wt% nano and micro silicon particles. Then, these powders were uniaxially pressed in a steel die into a disk, with thickness of 3.45 mm and diameter of 25 mm under 15MPa pressure. In the next stage, these specimens were sintered in a tube furnace (Exaction Model: BE-96) at 1100°C, 1200°C and 1300°C under N_2 atmosphere. The firing schedule organized a heating and cooling rate of 5°C/min with 2 h soaking time at the maximum temperature. The furnace atmosphere adjusted under flow of N_2 with rate of 20 lit/min. The furnace was allowed to cool by itself.

The crystalline phase of the sintered samples was identified by the X-ray diffraction (XRD) (Philips model: Expert) which was analyzed at 40 kV and 30 mA using a Cu K_α radiation. Finally, the morphological characteristics of Si_3N_4 reinforcements were explored by implementation of the image analyzing technique on micrographs taken by the scanning electron microscopy (SEM) (Spot Magn). The surface area was measured with the BET technique (Costech-Model: 1042) [15].

Results and Discussion

Thermal Analysis of Composite Si_3N_4-Cordiearite

Differential Thermal analysis (DTA) and thermogravimetry (TG) were carried out under N_2-atmosphere of the green compact of mixture raw cordierite and nano silicon to determine the temperature of nitridation reaction at a heating rate of 10°C/min (Fig. 1).

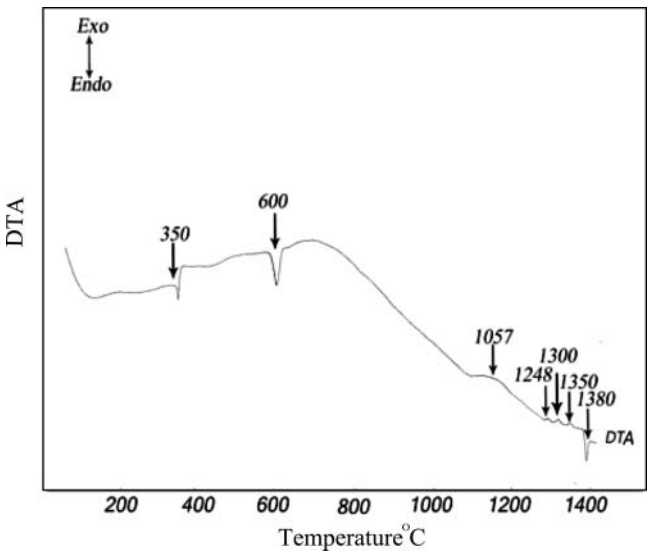

Figure 1. DTA-TG curves of green compact of cordierite and nano silicon powder at the nitrogen atmosphere.

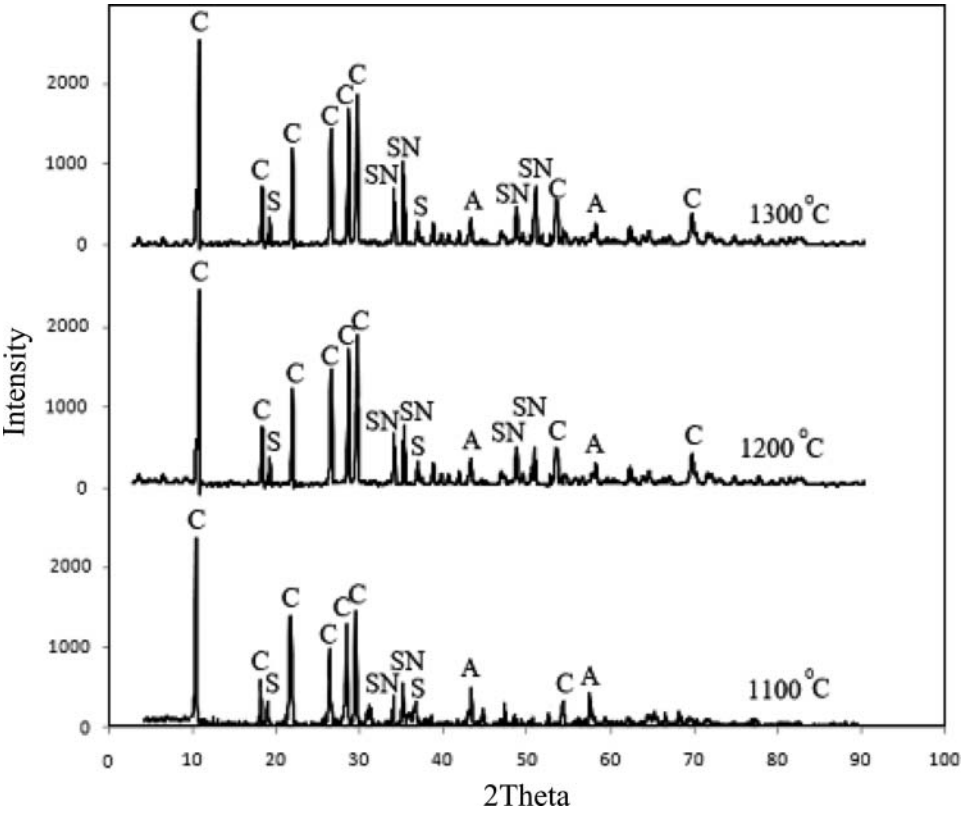

Figure 2. XRD patterns of Si_3N_4-cordierite composite, with 10% nano silicon particles at different temperature. C: Cordierite, SN: Silicon nitride, A: Corundum, S: Spinel.

The first endothermic peak at 350°C was attributed to the weight loss of constitutional water and the temperature for the second sharp endothermic peak around 600°C related to the dehydroxilation of kaolinite. A broad exothermic peak between 1100°C and 1200°C, corresponding to the nitridation of nano silicon particles, could be related to the phase composition of the sample sintered at 1100°C. As shown in Fig. 2, Si_3N_4, cordierite, spinel and corundum peaks are available at sintering temperature of 1100°C, while no other new phases have formed upon 1100°C. Using nano silicon powder showed an important effect on the nitridation process for the synthesis of Si_3N_4 by decreasing the process temperature. On the other hand three small exothermic peaks at about 1248°C, 1300°C and 1345°C were detected. These peaks according to the work by Shi et al. could be related to the formation of cordierite phase [16]. An endothermic peak at 1349°C in DTA curve is related to the formation of glass phase of silicon. According to the above results and XRD pattern (Fig. 2), will be illustrated in the next section, the following reaction during nitridation could be concluded:

$$3Si + 2N_2 \rightarrow Si_3N_4 \quad (1)$$

$$MgO + Al_2O_3 \rightarrow MgO \cdot Al_2O_3 \text{ (spinel)} \quad (2)$$

$$2MgO + 2Al_2O_3 + 5SiO_2 \rightarrow 2MgO \cdot 2Al_2O_3 \cdot 5SiO_2 \text{ (cordierite)} \quad (3)$$

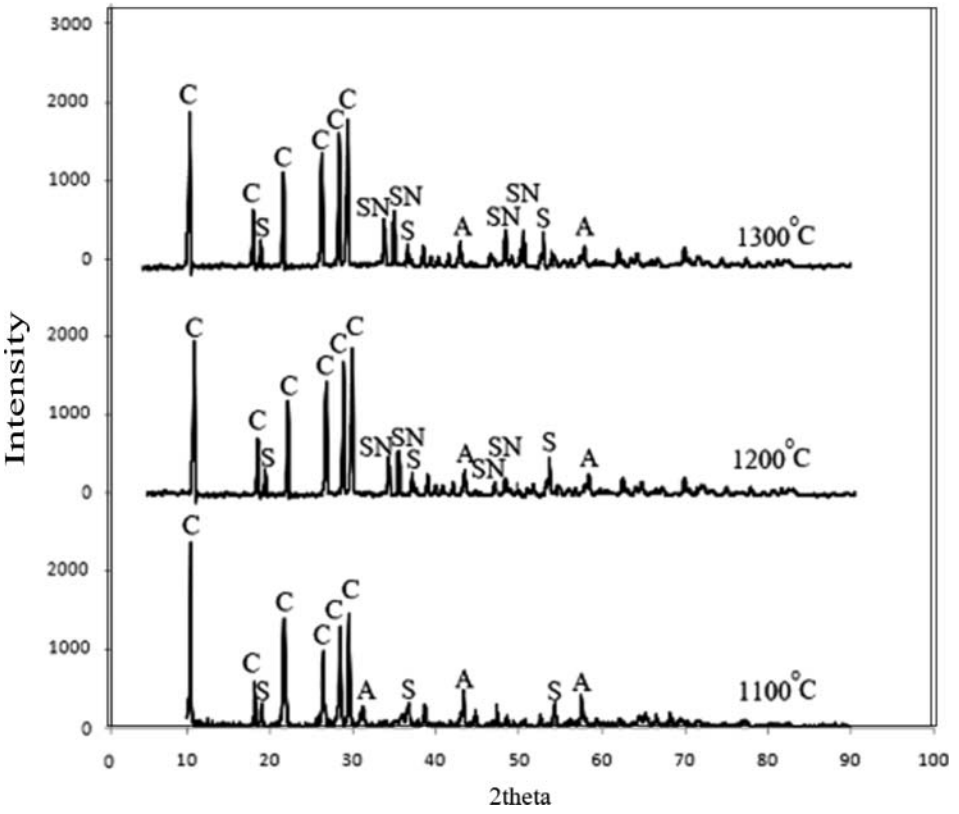

Figure 3. XRD patterns of Si_3N_4-cordierite composite, with 10% micro silicon particles at different temperature. C: Cordierite, SN: Silicon nitride, A: Corundum, S: Spinel.

The Effect of Nano and Micro Silicon Powder on the Phase Analysis of Composite

Figures 2 and 3 show the XRD patterns of the Si_3N_4-cordiearite composite, with 10 wt% nano and micro silicon powder, sintered at 1100°C to 1300°C by increasing rate of 100°C in each step. In these patterns cordierite(C) was added as a main phase, and silicon nitride (SN), corundum (A) and spinel(S) ($2MgO \cdot Al_2O_3$) were formed as a crystallized phase by in situ formation process. The intensity of Si_3N_4 peaks increased with increasing firing temperature. Indeed, the intensity peaks of Si_3N_4 with nano silicon powder are more than micro silicon powder.

It has also observed that by using nano size silicon powder at firing temperature of 900°C, there is some evidence of Si_3N_4 formation in the XRD pattern (Fig. 4), while by using micro silicon powder, the nitride phase is not seen.

These phenomena could be related to the use of nano-sized silicon powder during sintering of composite under N_2 atmosphere. In fact, by using nano-sized silicon powder diminishes the firing temperature of silicon nitride. These phenomena can be helped to prevent cordierite melting during firing.

It is possible to confirm that a change in silicon starting particle size leads to a complete change of reaction during nitridation. This is indicating that nano-sized grain has a large reactive surface area improving the contact between nano silicon particles and nitrogen

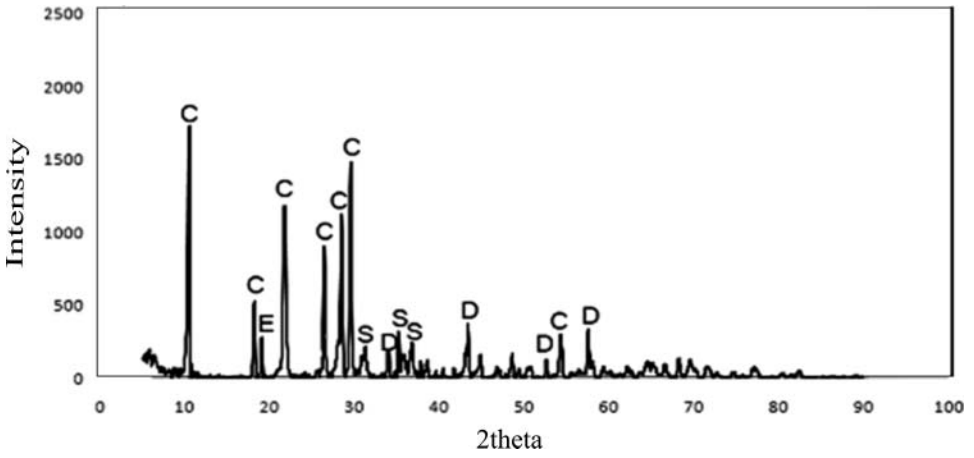

Figure 4. XRD patterns of Si_3N_4-cordierite composite, at 900°C. C: Cordierite, S: Silicon nitride, D: Corundum, C: Spinel.

gas. This can be resulted in an improved reaction rate and increased growth rate of Si_3N_4 crystals.

Effect of Different Size of Silicon on Density and Porosity

The variation of density and porosity of Si_3N_4-cordiearite composites is shown in Fig. 5. As can be seen in Fig. 5, by increasing the temperature, the density of composite decreases consequently. This phenomenon could be related to Si_3N_4 formation and volume expansion of this phase during nitridation. Also it is obvious that the reduction rate of density in sample with nano silicon powder is higher than sample prepared using micro silicon powder.

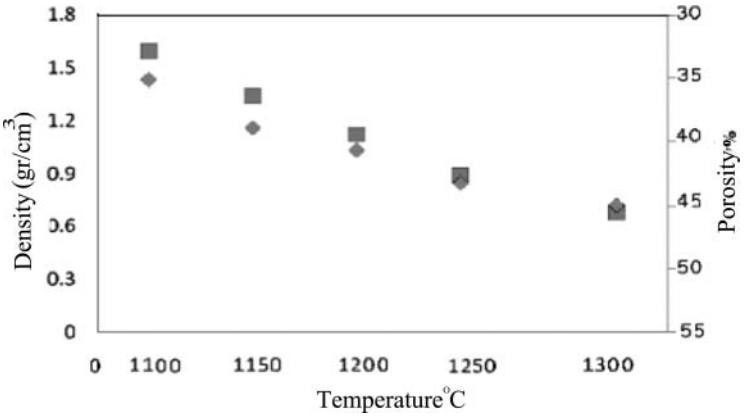

Figure 5. Variation of the density and porosity of Si_3N_4-Cordierite composite with 10% nano and mircro silicon particles. Samples were isothermally heated at different temperature for 9 h at nitrogen atmosphere. ■ nano; ◇ micron.

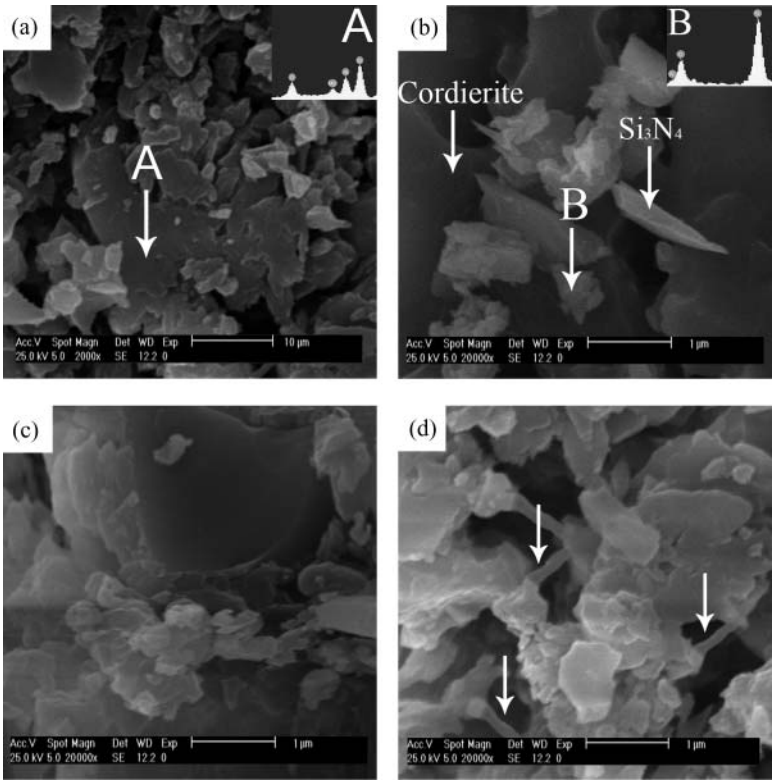

Figure 6. Scanning electron micrographs of sample Si_3N_4-cordierite composite with 10% nano silicon powder sintered at (a) and (b) 1100°C, (c) and (d) 1300°C.

Effects of Nano Silicon Powder on the Microstructure of Optimized Si_3N_4-Cordierite Composite

Figure 6 shows microstructures of Si_3N_4-Cordierite Composite at different temperatures with EDS analysis. According to EDS spectrums, the white area and gray area are related to nitride and cordierite phases respectively Fig. 6(a, b).

Figure 6(a, b) shows the formation of nitride phase on the surface of coarse cordierite aggregate with equiaxed morphology of nitride phase, by increasing firing temperature up to 1300°C which is closed to melting of cordierite aggregate. The different types of nitride phase with various morphologies were observed. The formation of these morphologies as shown in Fig. 6(c, d) could be related to the SDP (solution-diffusion-precipitation) mechanism [16]. Formation of needle shape of nitride phase confirmed that the liquid phase formation in this system was around temperature 1300°C and it was good evidence to apply nano silicon powder to decrease nitridation temperature.

Conclusions

The formation of in situ Si_3N_4 in the cordierite composite was successfully fabricated in nitrogen atmosphere by the reaction bonding technique from cordierite and nano silicon powder. The effect of nano silicon powder on the microstructure of Si_3N_4 grains, which

have a fine matrix grains at low sintering temperature, associated with increased specific surface area (12–13 m^2/g) resulted in enhancing the degree of reaction at low temperature. The average diameter in the Si_3N_4 crystals is strongly influenced by the particle size and distribution of the silicon particles. It was found that micro and nano silicon particles have different effects with the nitrogen in the matrix of cordierite at various temperatures. It is possible to synthesis high porosity in a cordierite- Si_3N_4 composite material with uniform microstructure. The pore size and porosity were strongly dependent on the silicon size and volume increment respectively.

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