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Effect of Y_2O_3 addition on ammono sol–gel synthesis and sintering of Si_3N_4–SiC nanocomposite powder

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Abstract

An ammono sol–gel and carbothermal reduction process was employed to prepare silicon nitride–silicon carbide (Si_3N_4–SiC) nanocomposite powder using silica sol, urea and carbon black as starting materials. When yttria (Y_2O_3) was introduced into the silica sol, a Si_3N_4–SiC–Y_2O_3 composite powder was obtained. Results showed Y_2O_3 addition led to substantial change in the synthesizing temperature and the morpyology and size of Si_3N_4–SiC powder. The state of Y presented in Si_3N_4–SiC composite powder was investigated by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The effect of addition method and amount of additives on densification and microstructure of sintered Si_3N_4–SiC ceramics was examined. In comparison with mixed powders of Si_3N_4–SiC and Y_2O_3, the evaluated densification of Si_3N_4–SiC–Y_2O_3 composite powder can be carried out with a smaller amount of Y_2O_3, since Y_2O_3 was dispersed more homogeneously with Si_3N_4–SiC.

Keywords: A. Powder: chemical preparation; A. Sintering; A. Sol–gel process; D. SiC; D. Si_3N_4; D. Y_2O_3

1. Introduction

Silicon nitride (Si_3N_4) is one of the most promising ceramic materials for high-temperature structural applications. In order to further improve its strength and toughness, many methods have been proposed, including second-phase strengthening and self-strengthening [1–6]. Among them is a method that involves the dispersion of ultrafine SiC particles inside the grains or at the grain boundaries of a Si_3N_4 matrix, that can lead to an improvement in the mechanical response of the material at both room and elevated temperatures. Fabrication of Si_3N_4–SiC involves a series of process steps, including synthesis of the Si_3N_4–SiC composite powder, mixing and milling for consolidation of powder, shaping, and sintering. In order to obtain high-performance Si_3N_4–SiC composites, the ideal powders for fabricating Si_3N_4–SiC components should have high purity, non-agglomeration, fine particle size with narrow size distribution, and equiaxed morphologies.

A number of processes exist for producing Si_3N_4–SiC composite powders. These approaches include chemical vapor deposition (CVD) to make amorphous Si–N–C powders [7,8], pyrolysis of organic precursors [9,10], partial reduction of Si_3N_4 by carbon to produce SiC nanoparticles [11,12], carbothermal reduction of SiO_2 in the presence of nitrogen [13], and mechanical mixing of Si_3N_4 and SiC powders [14]. Among the preparation methods, the carbothermal reduction of SiO_2 has attracted enormous interest, because the cost of the raw materials is relatively low and simultaneous synthesis of Si_3N_4 and SiC guarantees that the SiC particles are inherently well distributed. Sol–gel and carbothermal reduction processing has been considered to be an attractive method of synthesizing homogeneous and ultrafine powders [15–18]. Another advantage of sol–gel processing is that, because the raw materials are in solution, trace elements can be easily introduced into the solution by adding the elements in the form of organometallic compounds or soluble organic or inorganic salts. Such trace elements can be important in

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improving the rate of synthesis or in adjusting the microstructure of the powders.

On the other hand, since Si_3N_4 and SiC are compounds with strong covalent bonds, it is difficult to obtain high dense Si_3N_4–SiC ceramics without sintering additives. The addition of oxides, however, has a negative effect on the high-temperature strength of sintered materials because the additives remain in a grain-boundary glass phase [19–22]. From the viewpoint of mechanical properties at elevated temperature it is preferable to reduce the use of sintering aids to a minimum. Yttria (Y_2O_3) is known as one of the most effective sintering additives for Si_3N_4–SiC powders [23,24]. In order to achieve good mixing of the starting materials and excellent chemical homogeneity of the final product, many researchers have used alkoxides and inorganic salts as starting materials for sintering purpose by various wet-chemical methods [25–27]. However, little attention has been paid to the influences of the introduction of the additive (Y_2O_3) into raw materials on the synthesis and sinterability of Si_3N_4–SiC powders, where the additive may act as a sintering aid. Based on our previous studies [28] and with the aim of preparing high-quality, low cost powders and decreasing the amount of additive, a novel ammono sol–gel processing was tried for the synthesis of Si_3N_4–SiC and Si_3N_4–SiC–Y_2O_3 composite powders. Densification was carried out by hot pressing and sintering behavior was investigated.

2. Experimental

Commercial silica sol (modified water glass by ion-exchange, 26–28% SiO_2) (Hunan Chemical Co., China), urea, yttrium nitrate (AR grade, Shanghai Chemical Co., China) and carbon black (surface area: 120–150m^2/g) were used as starting materials. Urea was dissolved in water and mixed homogeneously with silica sol, and the aqueous solution was slowly heated to 80 °C, then bubbled with ammonia under continuous stirring until the solution became strongly viscous. After drying, a gelled precursor was readily obtained. When yttrium nitrate was introduced into silica sol, a precursor containing yttrium was obtained by the same method. The precursors were resolved in ethanol and mixed with carbon black by ball milling in a plastic jar with agate balls for 4 h. The mixture was dried at 120 °C, then placed in a graphite pot and heated at 1450–1650 °C in flowing nitrogen atmosphere for the synthesis of Si_3N_4–SiC (Y_2O_3) by carbothermal reduction. Residual carbon in the synthesized powders was removed at 600 °C in air. The final products were characterized by X-ray diffractometry (XRD) with Co Kα radiation (Model D5000, Siemens), X-ray photoeletron spectroscopic (XPS) and transmission electron microscopy (TEM) (Model H800, Hitachi).

Yttria (Y_2O_3, 99.9% pure, Hunan Institute of Rare Earth, China) was used as the sintering aid for Si_3N_4–SiC powders. The amount of Y_2O_3 addition was varied from 4 to 14 wt.%. The mixture powders of Si_3N_4–SiC (25%) with Y_2O_3, and Si_3N_4–SiC (25%)-Y_2O_3 composite powders were mixed by ball milling with ethanol in a plastic pot for 24 h, respectively. The slurries were dried and then sieved to particle size smaller than 48 μm. The mixtures were cold pressed at 25 MPa. The compacts were then subjected to hot pressed at 1700 °C for 30 min in a nitrogen atmosphere under a pressure of 20 MPa. The heating rate was 30 °C/min, and the cooling rate was 60 °C/min from 1700 to 1200 °C. Sintered density was measured by the Archimedes method. The theoretical densities of the specimens were calculated according to the rule of mixtures. Phase identification of the samples was performed by XRD. The microstructure was observed by scanning electron microscopy (SEM) using polished specimens etched in molten NaOH.

3. Results and discussion

3.1. Ammono sol–gel synthesis of Si_3N_4–SiC powders

XRD patterns of the powders synthesized in nitrogen atmosphere at different temperatures are shown in Fig. 1. At 1500 °C, a complete carbothermal nitridation of SiO_2 occured and only Si_3N_4 was observed. At 1530 °C, SiC was observed. SiC content of Si_3N_4–SiC powders increased with the increase of temperature. At a temperature of 1620 °C, only SiC was observed. In comparison the system without ammono silica [28], ammonolysis activated the reaction of carbothermal nitridation. Fig. 2 shows IR spectra of ammono precursor, silica gel and urea. In the IR spectrum of the silica gel, the strong absorption peak at about 3500 cm^{-1} was related to the $-$OH stretching vibration. We find that the OH group in the precursor was weakened, and the NH_4 group was observed. These results suggested that ammonolysis of the aqueous solution of silica sol and urea led to dehydration of silica sol during the gelling process, which might prevent the formation of agglomerates and produce very fine gel particles because of the destruction of the Si–O–Si net. The new process increased the reactivity of the reactants and enhanced the Si_3N_4–SiC formation.

Fig. 3 shows the TEM micrographs of Si_3N_4–SiC powders produced at 1550 °C. It can be seen that the hexagonal prisms were silicon nitride with a size of 50–60 nm, while the smaller particles were silicon carbide, which was confirmed by electron diffraction. SiC particles were produced by the reaction between Si_3N_4 and residual carbon in this process.

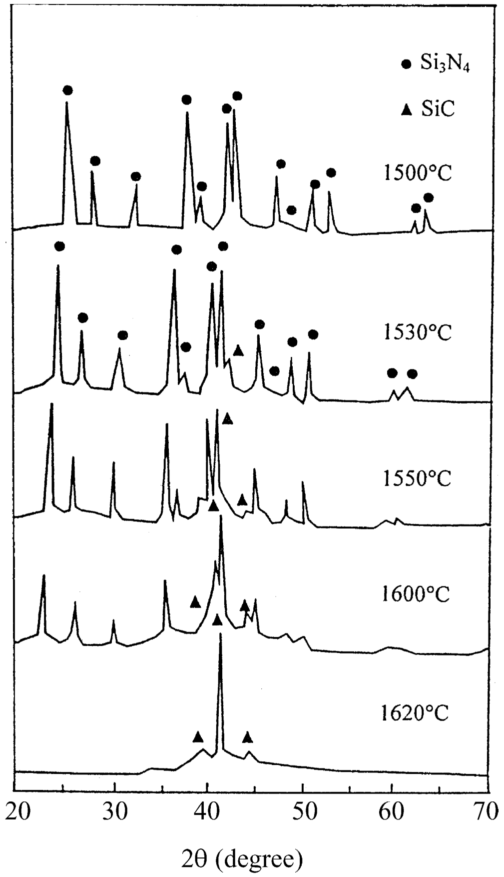


Fig. 1. XRD patterns of the powders at different nitridation temperatures.

3.2. *Effect of Y_2O_3 additive on synthesis of Si_3N_4–SiC powders*

When yttrium nitrate (corresponding to 8 wt.% Y_2O_3 for Si_3N_4–SiC) was introduced into the silica sol, yttrium mixed homogeneously with silica through the ammono sol–gel process. The addition of Y_2O_3 resulted in a decrease of synthesizing temperature of Si_3N_4–SiC powders during carbotheraml reduction. An X-ray diffraction pattern of the powders synthesized at 1500 °C (Fig. 4) exhibited only α-Si_3N_4, β-SiC and Y_2O_3 phase. Yttrium silicate was not identified; this is probably because its concentration is too low, or present as a solid solution. At the same time Si_3N_4 and SiC peaks slightly shifted towards a larger 2θ angle. The change in lattice constants means yttrium entered into the lattice of Si_3N_4 or SiC.

Fig. 5 shows the TEM micrograph of Si_3N_4–SiC–Y_2O_3 composite powders. The micrograph obtained from the system with oxide addition at 1500 °C shows that a SiC whisker was formed and the Si_3N_4 particle size increased to 70–80 nm. The reason for the formation of whiskers could be that due to the existence of rare earth element in SiC lattice, the activation energy for SiC growth decreased and the growth of SiC was improved to some special direction, so as to form whisker, which was confirmed by electron diffraction. At the same time, Y_2O_3 addition may result in formation of a liquid phase to promote the growth of whiskers and particles. This was in agreement with promotion of carbothermal reduction under the additive. When the reaction temperature increased to 1550 °C, XRD analysis demonstrated that the product powder was composed of β-SiC and tiny amount of Y_2O_3. The synthesis temperature is at least 50 °C lower than the case without the additive. However, increasing of yttrium nitrate concentration further had no additional influence on the carbothermal reduction process.

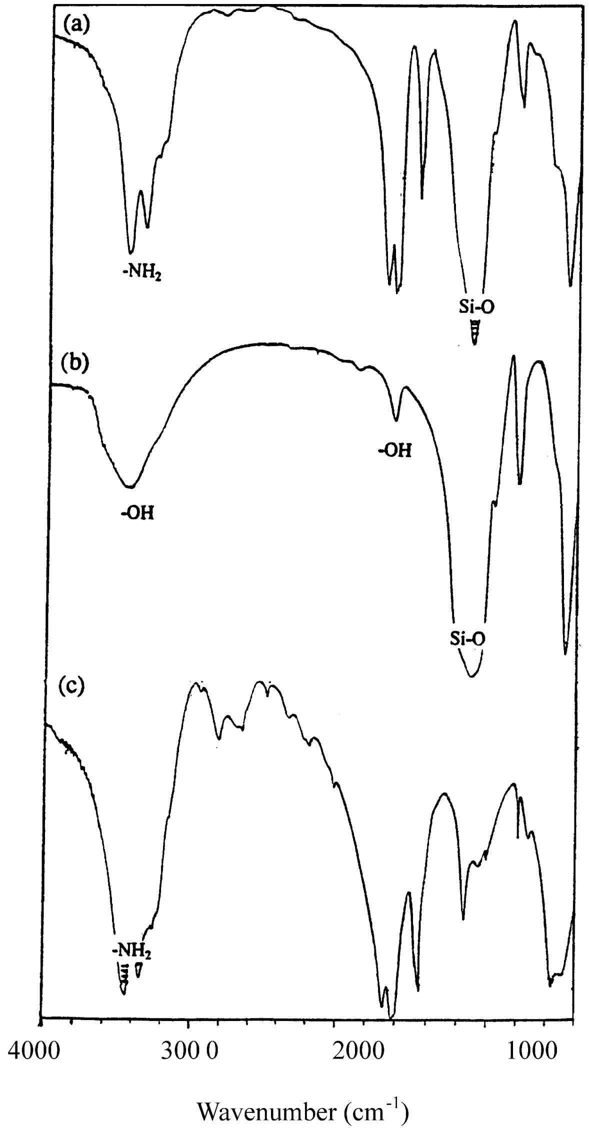


Fig. 2. Infrared spectra of (a) ammono precursor, (b) silica gel, (c) urea.

In order to investigate the structure of composite powders and the state of yttrium in the powders, XPS measurements of Si_3N_4, Si_3N_4–SiC (Y_2O_3) and SiC powders were conducted and the results are shown in

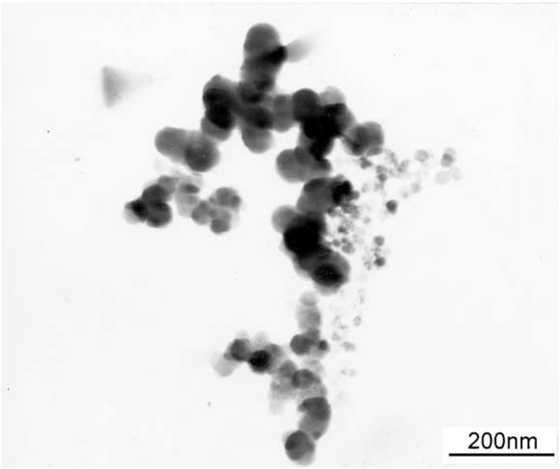


Fig. 3. TEM micrographs of Si_3N_4–SiC powders obtained at 1550 °C.

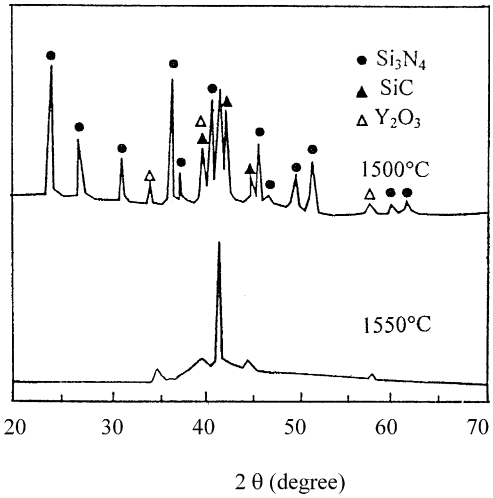


Fig. 4. XRD patterns of the powders prepared from the system with additive at different nitridation temperatures.

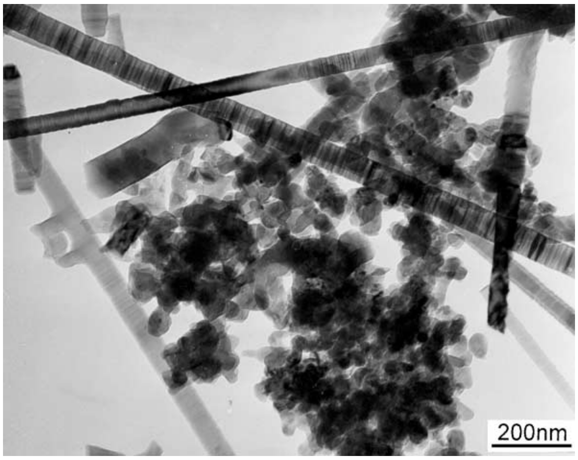


Fig. 5. TEM micrographs of powders obtained from the system with additive at 1500 °C.

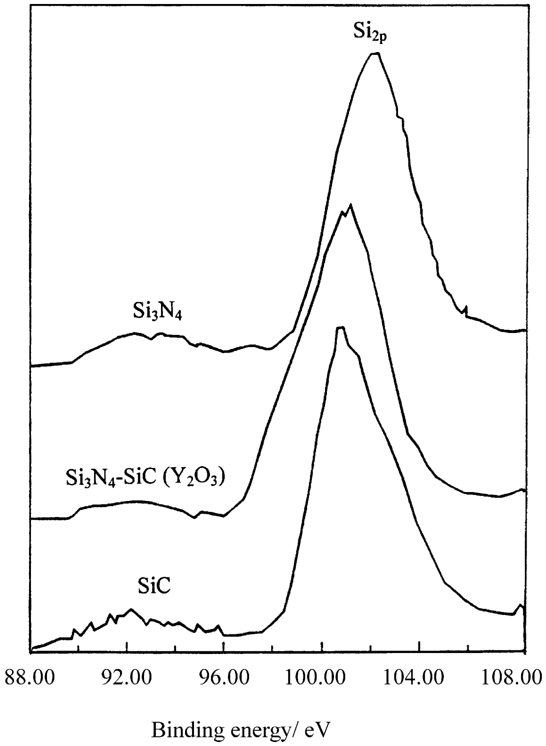


Fig. 6. Si_{2p} XPS spectra of Si_3N_4, Si_3N_4–SiC (Y_2O_3) and SiC.

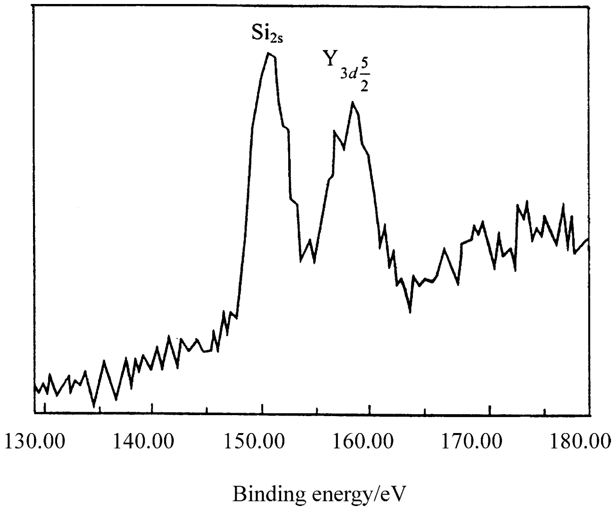


Fig. 7. $Y_{3d\frac{5}{2}}$XPS spectra of Si_3N_4–SiC (Y_2O_3) .

Figs. 6 and 7. Si_{2p} peaks for Si_3N_4 and SiC were observed at 102.4 eV and 100.5 eV, respectively. In the case of Si_3N_4–SiC composite powders, the Si_{2p} peak was a single peak at 101.2 eV. It has been shown that the Si_{2p} spectra of the mixed powders consisted of SiC and Si_3N_4 peaks, and that their intensities depend on the composition [29]. This result suggested that the chemical state of Si in the composite powder was different from that in the mechanically mixed powders. The chemical shift appearing in the XPS spectra is mainly due to the electric charge distribution around the atoms. It was

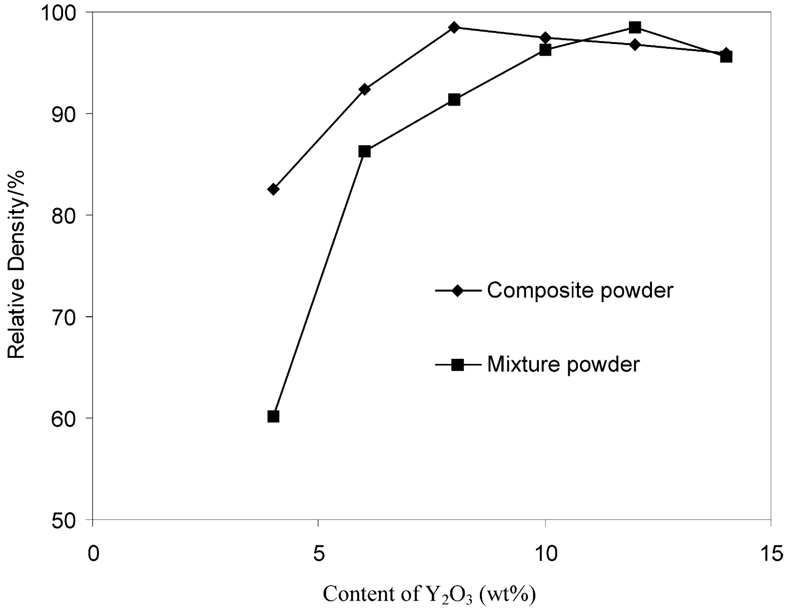
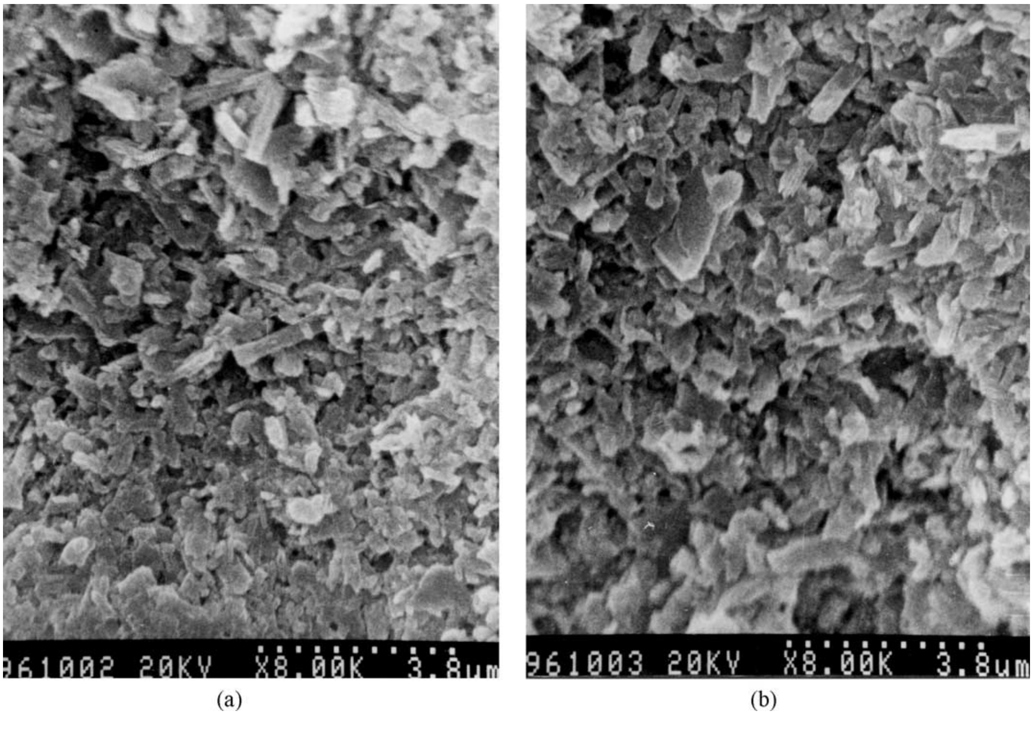


Fig. 8. Relative density of hot pressed Si_3N_4–SiC specimens from different powders versus content of additive Y_2O_3 at 1700 °C.



(a) (b)

Fig. 9. SEM micrographs of Si_3N_4–SiC compacts after etching in molten NaOH, hot pressed using: (a) composite powder, (b) mixture powder.

assumed that silicon atoms were surrounded by both nitrogen and carbon atoms, Si, C, and N atoms were intimately mixed in the composite powders. The Si_3N_4 phase in the composite powders dissolved carbon. The SiC phase in the composite powders also dissolved nitrogen. The $Y_{3d_{\frac{5}{2}}}$ spectra of Si_3N_4–SiC–Y_2O_3 composite powder contains a single peak at 157.5 eV, different from the binding energy of the Y_2O_3 compound, with a charge shift of 1 eV. Since the XRD results for composite powders showed crystalline Y_2O_3 patterns, these results suggested that the dissolution of part of the yttrium into the lattice resulted in the change in binding energy.

3.3. Sintering behavior and microstructure of Si_3N_4–SiC

Fig. 8 illustrates the relationship between the bulk density of Si_3N_4–25%SiC composites and the Y_2O_3

content. For the Si_3N_4–SiC–Y_2O_3 composite powders, the density increased with increasing the amount of Y_2O_3 and a nearly full dense Si_3N_4–SiC composite was obtained when the amount of Y_2O_3 was increased to 8 wt.%. However, full densification of the mixture powders of Si_3N_4–SiC and Y_2O_3 at the same sintering temperature and pressure required the addition of 12 wt.% Y_2O_3. The discrepancy in the sintering densification between composite powders and mixture powders, as shown in Fig. 8, is contributed by the inhomogeneous mixing with the sintering additives. Present results suggest that homogeneous mixing is very important for correct densification, because liquid-phase sintering of Si_3N_4–SiC composites is a topochemical reaction. The liquid phases that are expected to form during hot pressing of Si_3N_4–SiC would assist in the rearrangement of grains, thereby leading to increased densification. However, the formation routes of liquid phases for the Si_3N_4–SiC–Y_2O_3 green powder sample may be not the same as those for the Si_3N_4–SiC+Y_2O_3 sample. In Si_3N_4–SiC–Y_2O_3 system, the starting Si_3N_4 and SiC particles may be coated by Y_2O_3 films and dissolved the part of yttrium. The liquid phases formed during hot pressing would appear to spread quickly over the grain-boundary region, wet and penetrate among solid particles, in order to help rearrangement of the grains towards a more closely packed configuration. A smaller amount of Y_2O_3 would form the sufficient volume fraction of liquid to wet Si3N4 and SiC effectively and it has appreciable solubility of Si_3N_4–SiC at sintering temperature, since Y_2O_3 was dispersed more homogeneously with Si_3N_4–SiC than that by mechanical mixing.

SEM micrographs of the dense Si_3N_4–SiC samples hot pressed using the composite powders (corresponding to 8 wt.% Y_2O_3 for Si_3N_4–SiC) and the mixture powders (12 wt.% Y_2O_3 for Si_3N_4–SiC) are shown in Fig. 9 (a) and (b), respectively. Although the SEM micrographs and XRD measurements showed that both hot pressed compacts consisted of fine-textured Si_3N_4 and SiC grains, a significant difference in morphology was apparent between them. It can be seen from Fig. 9 that the grain-boundary glass phase of the sintered compact from Si_3N_4–SiC–Y_2O_3 composite powders is less than that from mixture powders of Si_3N_4–SiC and Y_2O_3, since the sintering additive decreased.

4. Conclusion

Si_3N_4–SiC nanocomposite powders were successfully prepared by the process of ammono sol–gel and carbothermal reduction using silica sol, urea and carbon black. Ammonolysis can increase the reactivity of the reactants and enhanced the Si_3N_4–SiC formation. Si_3N_4–SiC–Y_2O_3 nanocomposite powders were obtained with the same method by introducing yttrium nitrate into silica sol. The addition of Y_2O_3 resulted in a decrease of synthesis temperature of Si_3N_4–SiC powder and formation of a SiC whisker. The results of XRD and XPS showed the dissolution of part of the yttrium into the lattice. The remaining Y existed in the composite powders as Y_2O_3. The Si_3N_4–SiC–Y_2O_3 powder is easily sintered, and this results in decrease in the amounts of sintering additive and grain-boundary glass phase in Si_3N_4–SiC ceramics.

Acknowledgements

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