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Crystallization of MgO during sintering of silicon nitride with magnesia and ceria

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This paper deals with the crystallization of MgO during sintering of Si_3N_4-MgO-CeO_2 ceramics. At the initial stage of sintering (1450–1550 °C), MgO-CeO_2 reacts with free silica to form sufficient liquid phase to densify Si_3N_4 into nearly full density ceramics; at final stage (1600–1800 °C), the crystallization of MgO reduces the amount of glassy phase which is harmful to the high-temperature properties. MgO-CeO_2 is found to be an excellent sintering aid for Si_3N_4. © *1999 Kluwer Academic Publishers*

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1. Introduction

Silicon nitride ceramic materials show great potential for wide applications. Sintering is a very cost-effective way to produce silicon nitride ceramics. However, it is difficult to densify pure silicon nitride due to its covalent nature of bonding. Metal oxides such as MgO [1, 2], Al_2O_3 [3, 4], and rare-earth oxides [5–7] have been found to be effective sintering aids for Si_3N_4. Silicon nitride is also limited in its high-temperature properties due to glassy phases formed at the grain boundaries as a result of processing with sintering aids. Two main ways have been studied to address this problem: (1) the crystallization of the glassy phase by postsintering heat treatment [8]; (2) the formation of a solid solution, i.e., sialon [9]. However, the stresses resulting from the postsintering heat treatment process decrease the room-temperature as well as the high-temperature strength and monophase Si_3N_4 solid solution ceramic materials exhibit a low fracture toughness. This paper discusses the crystallization of MgO during the sintering of Si_3N_4-MgO-CeO_2 ceramics. The present work shows that MgO-CeO_2 is an excellent sintering aid, which leads to high strength and a less glassy phase for the sintered Si_3N_4-MgO-CeO_2 ceramics.

2. Experimental

Composition of (90 wt %Si_3N_4[†] + 5 wt %MgO[‡] + 5 wt %CeO_2[§]) was chosen for this study. Powder mixtures were ball milled in anhydrous alcohol for 24 hours with WC-6%Co cemented carbide medium and container. After they were milled, the powder mixtures were dried, shifted, dry-pressed into bars in a steel die at 120 MPa. The compact samples were embedded in a Si_3N_4 + 50 wt %BN mixed-powder-bed in a molybdenum crucible. Pressureless sintering was conducted in a graphite vacuum furnace backfilled with 1 atm nitrogen gas at 1450, 1500, 1600 and 1800 °C for 1 hour, respectively.

Phase identification was made by X-ray diffraction using CuK_α radiation. TEM specimens were prepared in the usual way by cutting, grinding and finally ion beam thinning. A H-800 transmission electron microscope fitted with an EDAX was used for TEM work.

3. Results and discussion

Fig. 1 shows the XRD pattern of the green compact of Si_3N_4 contained 5 wt %MgO + 5 wt %CeO_2. Before sintering, α-Si_3N_4, β-Si_3N_4, MgO, CeO_2 and WC existed in the green compact. Chemical analysis indicated that about 4 wt %WC was introduced by the milling process.

Fig. 2 shows the XRD pattern of a sintered body heated at 1800 °C for 60 min. Most of the α-Si_3N_4 has transformed into β-Si_3N_4, while CeO_2 has disappeared, and MgO remains.

The conclusion seems obvious that CeO_2 reacted with free silica to form a liquid phase at 1800 °C and was then transformed into a glassy phase after cooling down. MgO did not take part in the reaction.

According to MgO-SiO_2 phase diagram, there is an eutectic point at 1543 °C. So it seems impossible that MgO did not react with SiO_2 at 1800 °C. In order to have a better understanding of the unclear points involved, a series of experiments were designed. The sintering

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[†] Purchased from Zhuzhou Cemented Carbide Works, Zhuzhou 412000, People's Republic of China.

[‡] Purchased from Tianjing Chemicals, Tianjing 130020, People's Republic of China.

[§] Purchased from Hunan Rare Earth Institute, Changsha 41000, People's Republic of China.

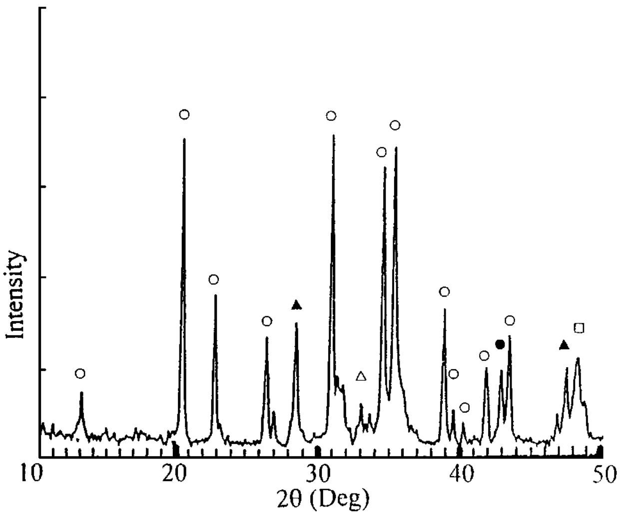

Figure 1 XRD pattern of the $Si_3N_4 + 5\%MgO + 5\%CeO_2$ green compact: (○) α-Si_3N_4, (△) β-Si_3N_4, (●) MgO, (▲) CeO_2, (□) WC.

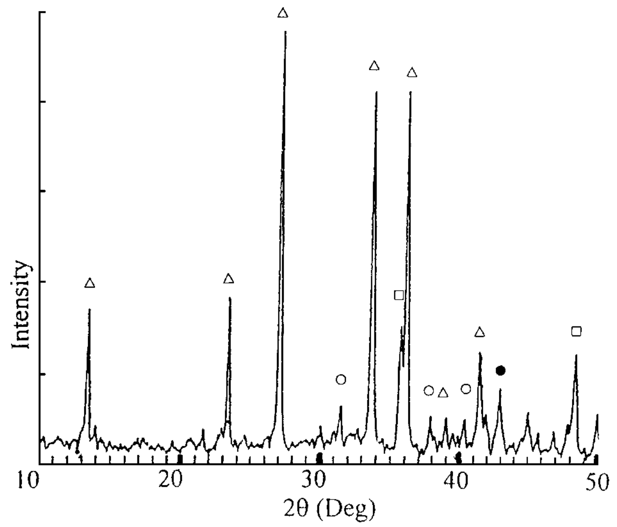

Figure 2 XRD pattern of the $Si_3N_4 + 5\%MgO + 5\%CeO_2$ ceramics sintered at 1800 °C for 60 min: (○) α-Si_3N_4, (△) β-Si_3N_4, (●) MgO, (▲) CeO_2, (□) WC.

temperatures were 1450, 1500, 1550, and 1600 °C, respectively.

Fig. 3 represents the XRD pattern for a specimen sintered at 1450 °C for 60 min. α-Si_3N_4, β-Si_3N_4 and WC peaks can be identified, but neither MgO nor CeO_2 is found.

Fig. 4 shows the XRD pattern for a specimen sintered at 1500 °C for 60 min. It is similar to Fig. 3 with no sign of MgO and CeO_2.

The XRD results for the specimens sintered at 1450–1500 °C suggest that both MgO and CeO_2 have reacted with free silica at 1450–1500 °C to form a liquid phase which was subsequently transformed into a glassy phase. This explains why they cannot be identified by X-ray diffraction.

In fact, the volume shrinkage for the specimen sintered at 1450 °C was about 36%, which indicated that a lot of liquid phase existed [10].

Fig. 5 represents the XRD pattern for a specimen sintered at 1550 °C. CeO_2 is absent. But MgO, which was absent formerly, is found again.

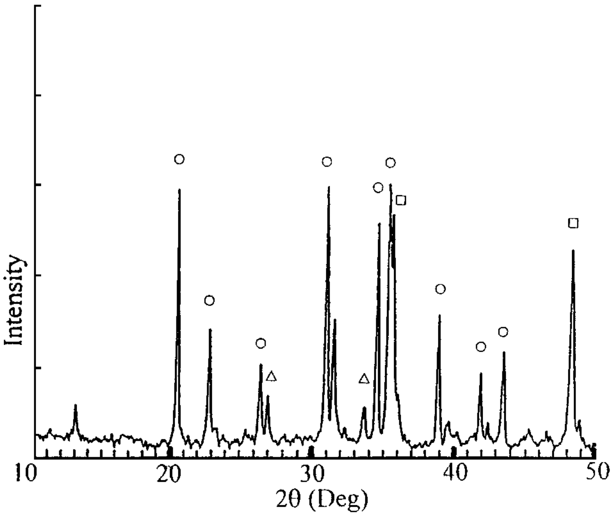

Figure 3 XRD pattern of the $Si_3N_4 + 5\%MgO + 5\%CeO_2$ ceramics sintered at 1450 °C for 60 min: (○) α-Si_3N_4, (△) β-Si_3N_4, (●) MgO, (▲) CeO_2, (□) WC.

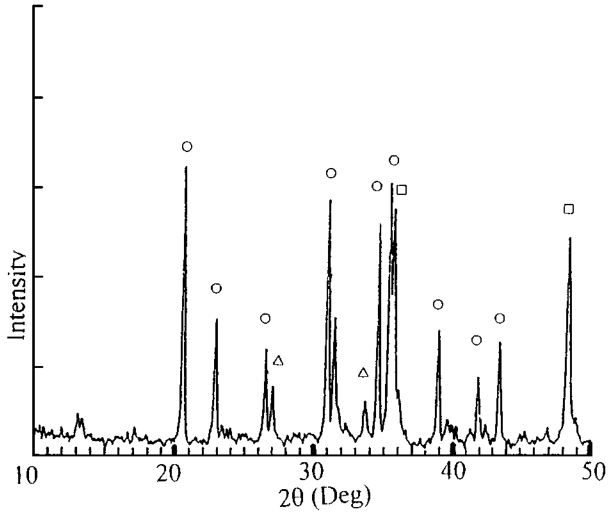

Figure 4 XRD pattern of the $Si_3N_4 + 5\%MgO + 5\%CeO_2$ ceramics sintered at 1500 °C for 60 min: (○) α-Si_3N_4, (△) β-Si_3N_4, (●) MgO, (▲) CeO_2, (□) WC.

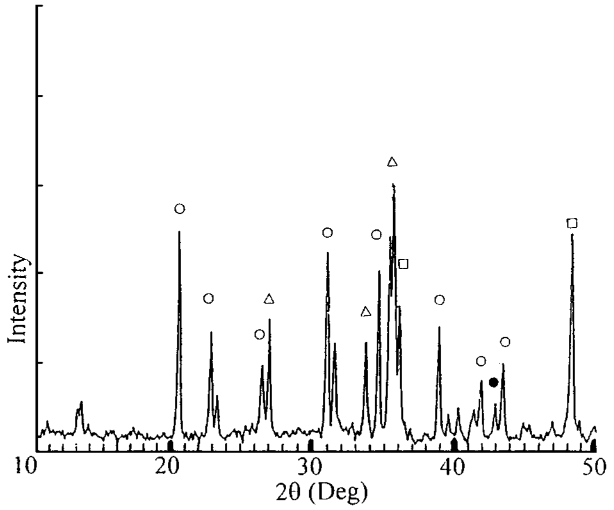

Figure 5 XRD pattern of the $Si_3N_4 + 5\%MgO + 5\%CeO_2$ ceramics sintered at 1550 °C for 60 min: (○) α-Si_3N_4, (△) β-Si_3N_4, (●) MgO, (▲) CeO_2, (□) WC.

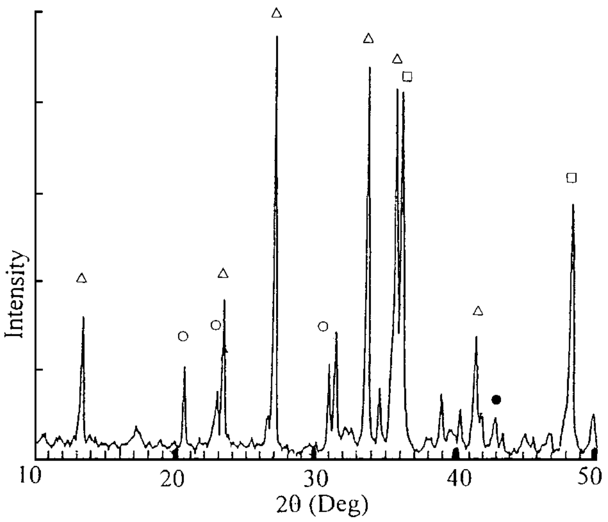

Figure 6 XRD pattern of the $Si_3N_4 + 5\%MgO + 5\%CeO_2$ ceramics sintered at 1600 °C for 60 min: (○) α-Si_3N_4, (△) β-Si_3N_4, (●) MgO, (▲) CeO_2, (□) WC.

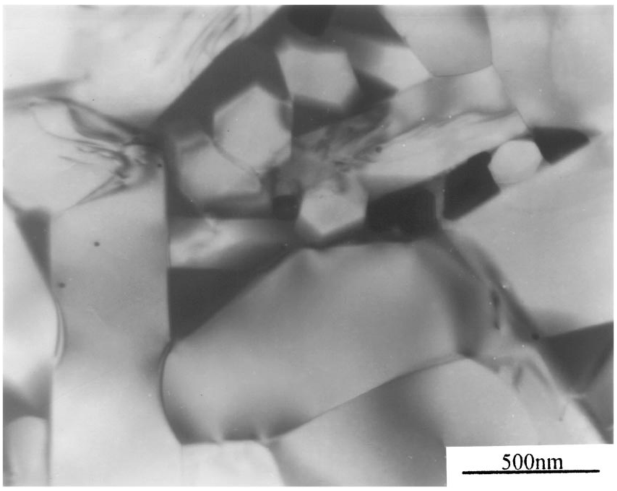

Figure 7 Typical microstructure of the $Si_3N_4 + 5\%MgO + 5\%CeO_2$ ceramics sintered at 1800 °C for 60 min.

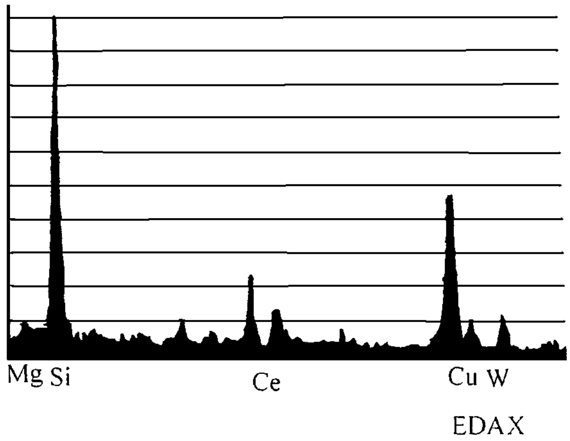

Figure 8 EDAX analysis on a glassy phase in $Si_3N_4 + 5\%MgO + 5\% CeO_2$ ceramics sintered at 1800 °C for 60 min.

Fig. 6 shows the XRD pattern for a specimen sintered at 1600 °C. It is similar to Fig. 5. There are no trances of CeO_2 and MgO is found.

The final interpretation could be given according to the below analysis.

For the Si_3N_4-MgO-CeO_2 system, MgO-CeO_2 reacts with free silica to form a liquid phase at a sintering temperature of 1450–1500 °C and is then transformed into a glassy phase after cooling down; above 1550 °C, MgO crystallizes during sintering. CeO_2 is in a glassy phase which hardly contains any MgO.

This particular phenomenon is of great value for the sintering of Si_3N_4. At the initial stage of sintering (1450–1550 °C), MgO-CeO_2 reacts with free silica to form sufficient liquid phase to densify Si_3N_4 into nearly full density ceramics (the pressureless sintered Si_3N_4-MgO-CeO_2 ceramics in the present study achieved a relative density of 98.5% and a strength of 950 MPa) [10]; at final stage (1600–1800 °C), the crystallization of MgO reduces the amount of glassy phase which is harmful to the high-temperature properties. The sintered Si_3N_4-MgO-CeO_2 ceramics contain little refractory Ce-rich silicate glassy phase. Thus, MgO-CeO_2 can be considered as an excellent sintering aid for Si_3N_4.

In fact, M. J. Hoffmann has found that the crystallization of additives can occur during sintering, especially for compositions directly on a tie line between a secondary phase and Si_3N_4. In this case, the volume fraction of the liquid phase is strongly reduced and complete densification is impossible [11].

Fig. 7 shows a typical microstructure of the silicon nitride sintered with $5\%MgO + 5\%CeO_2$ at 1800 °C for 60 min. The glassy phase remains at multigrain junctions as well as β-β Si_3N_4 grain boundaries. The glassy phase can be confirmed directly by its electron diffraction which appears to be an circle because of the absence of the Bragg diffraction. The result of the EDAX analysis of a glassy phase (Fig. 8) shows that Si, Ce are rich in the glassy phase but Mg is very poor (Mg: 0.64 at %, Si: 65.34 at %, Ce: 9.23 at %, Cu: 21.31 at %, W: 3.48 at %, Cu was introduced by specimen holder). This reveals that after sintering at 1800 °C, the main composition of the glassy phase in the sintered $Si_3N_4 + MgO + CeO_2$ ceramics is cerium silicate and hardly contains any MgO. This result is consistent with X-ray diffraction patterns.

4. Conclusions

(a) For the Si_3N_4-MgO-CeO_2 system, the MgO-CeO_2 seems to react with free silica to form a liquid phase at the sintering temperature of 1450–1550 °C and is then transformed into a glassy phase after cooling down; above 1550 °C, MgO crystallizes during sintering. Only CeO_2 is found in the glassy phase which hardly contains any MgO.

(b) MgO-CeO_2 is found to be an excellent sintering aid for Si_3N_4. At the initial stage of sintering (1450–1550 °C), MgO-CeO_2 reacts with free silica to form sufficient liquid phase to densify Si_3N_4 into nearly full density ceramics; at final stage (1600–1800 °C), the crystallization of MgO reduces the amount of glassy phase which is harmful to the high-temperature properties. The sintered Si_3N_4-MgO-CeO_2 ceramics contain little refractory Ce-rich silicate glassy phase.

Acknowledgements

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