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Short communication

Grain boundary glassy phase and abnormal grain growth of silicon nitride ceramics

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Abstract

The microstructure of pressureless sintered Si_3N_4 with MgO–CeO_2 additives has been studied by TEM. The grain boundary glassy phase is observed and confirmed directly by microdiffraction. EDAX analysis suggests that the main function of CeO_2 lies in the formation of a glassy phase, which contains hardly any MgO. This cerium silicate glassy phase is good to wet Si_3N_4. MgO–CeO_2 is an excellent sintering aid for Si_3N_4. Abnormal grain growth of Si_3N_4 occurred at a sintering temperature of above 1850°C, which leads to microcracks and dislocations and is harmful to mechanical properties.

Keywords: A. Sintering; B. Microstructure; D. Si_3N_4; Amorphous materials; TEM

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 into useful high strength ceramics 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 silicon nitride. Silicon nitride is also limited in its high-temperature properties due to the glassy phase formed at the grain boundaries as a result of processing with the sintering aids. This paper discusses the grain boundary glassy phase and abnormal grain growth of silicon nitride with a combination of ceria and magnesia additives — although they have both been extensively studied separately with silica.

2. Experimental

The composition of Si_3N_4 (Zhuzhou Cemented Carbide Works, China) + 5 wt.% MgO (Tianjing Chemicals, China) + 5 wt.% CeO_2 (Hunan Rare Earth Institute, China) was mixed and ball milled in alcohol for 24 h with WC–6% Co cemented carbide medium. The powder mixtures were dry pressed into bars in a steel die at 120 MPa. The compacts were embedded within a Si_3N_4 + 50 wt.% BN mixed-powder bed in a molybdenum crucible and pressureless sintered in a 1 atm N_2 atmosphere. Phase identification was made by X-ray diffraction (XRD) using CuK_α radiation. A H-800 transmission electron microscope fitted with an EDAX was used for TEM work. The TEM specimens were prepared in the usual way by cutting, grinding and finally ion beam thinning.

3. Results and discussion

3.1. Glassy phase

Fig. 1 shows a typical microstructure of the Si_3N_4 + 5% MgO + 5% CeO_2 ceramics sintered at 180°C for 60 min. The relative density and bending strength of the specimen are 98.5% and 1100 MPa, respectively. More details about this research are shown in our previous paper [8]. The glassy phase remains at multigrain junctions as well as β–β Si_3N_4 grain boundaries. The

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glassy phase can be confirmed directly by its electron diffraction, which appears to be an ambiguous circle because of the absence of the Bragg diffraction (Fig. 2). The result of the EDAX analysis of a glassy phase shows that Si, Ce are rich in the glassy phase but the amount of Mg is very low (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 $Si_3N_4+5\%$ $MgO+5\%$ CeO_2 ceramics is cerium silicate and hardly contains any MgO. This result is confirmed by XRD analysis. Fig. 3 shows the XRD pattern for the $Si_3N_4+5\%$ $MgO+5\%$ CeO_2 ceramics sintered at 1800°C for 60 min. There are no traces of CeO2, but MgO is found. Further investigation indicated that MgO did take part in the reaction to form a liquid phase at sintering temperature of 1450–1500°C.Above 1550°C, MgO would crystallize during sintering. More details about this research are shown in our previous work [9].

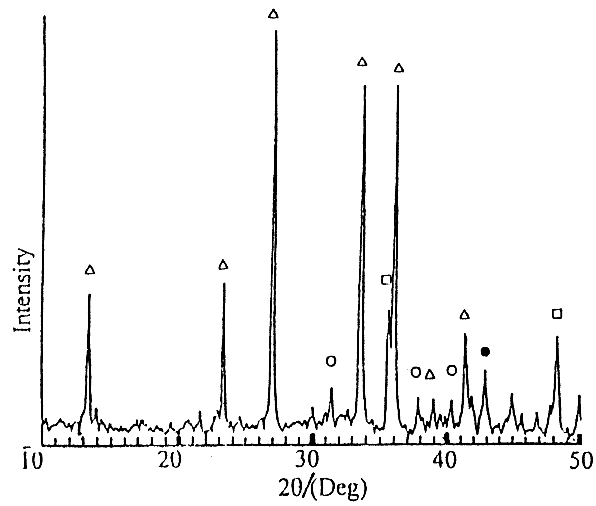

Fig. 3. XRD pattern of the $Si_3N_4+5\%$ $MgO+5\%$ CeO_2 ceramics sintered at 1800°C for 60 min: ○, α-Si_3N_4; △, β-Si_3N_4; ●, MgO; ▲, CeO_2; □, WC.

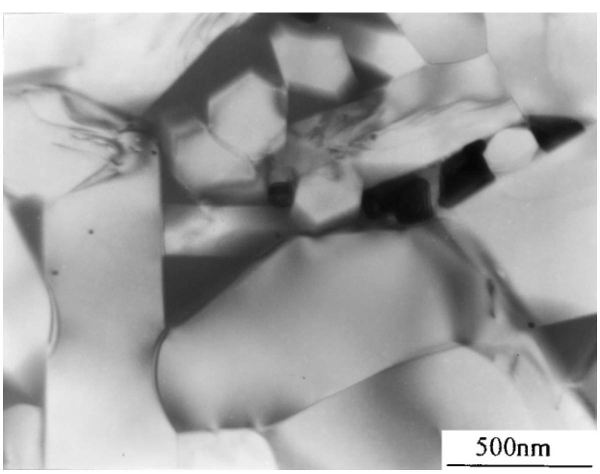

Fig. 1. Microstructure of the $Si_3N_4+5\%$ $MgO+5\%$ CeO_2 ceramics sintered at 1800°C for 60 min.

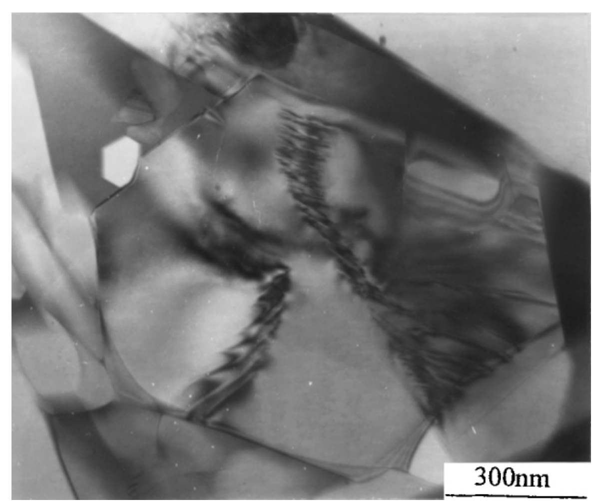

Fig. 4. Dislocations in an abnormal large grain.

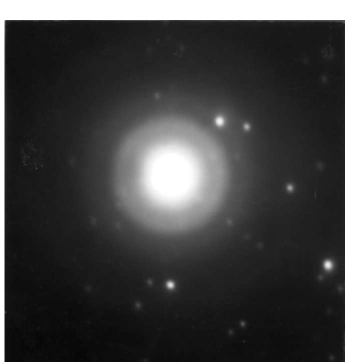

Fig. 2. Electron diffraction pattern of a glassy phase.

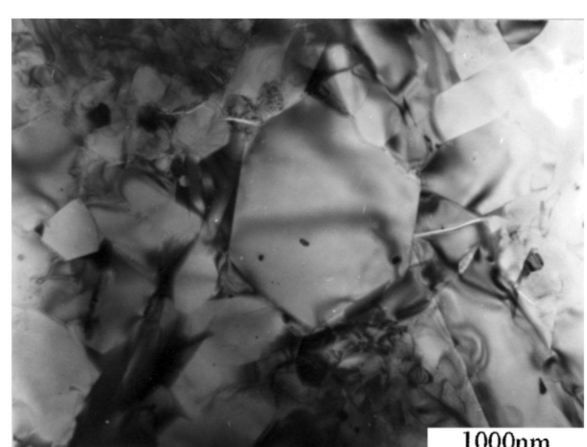

Fig. 5. Microcracks by an abnormal large grain.

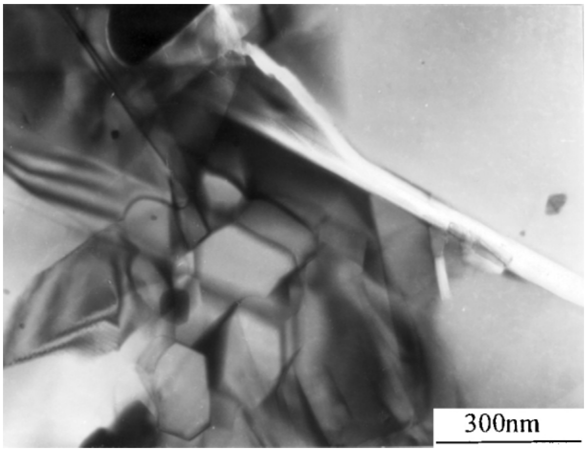

Fig. 6. Microcracks go through an abnormal large grain.

3.2. Abnormal grain growth

Prevention of abnormal grain (AGG) is often of high importance during sintering of high-strength ceramics. In the present study, AGG occurred at sintering temperatures of above 1850°C. AGG increase the grain boundary stress and leads to dislocations (Fig. 4) and microcracks (Figs. 5 and 6), which is harmful to the mechanical properties (the bending strength of the specimen is only 580 MPa). So, for Si_3N_4–MgO–CeO_2 system, the sintering temperature may not exceed 1800°C.

4. Conclusions

The main composition of the glassy phase in the sintered Si_3N_4–MgO–CeO_2 ceramics was cerium silicate and hardly contained any MgO. Abnormal grain growth occurred at sintering temperatures of above 1850°C, which led to microcracks and dislocations and was harmful to the mechanical properties.

Acknowledgements

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