

Influence of additives on microstructural changes in nitride bonded SiC refractories

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Abstract

In this study the microstructural development of nitride-bonded SiC refractories is reported in presence of Al₂O₃ and MgO. The samples were prepared by mixing, shaping and firing at 1450–1600 °C in a controlled atmosphere furnace. Phase analysis, microscopic observation and mechanical evaluation were taken as criteria for microstructural evolution.

The strength of samples doped with alumina was initially increased and then decreased at higher amount of alumina additions while the addition of magnesia decreased the strength. These phenomena could be attributed to microstructural evolution and mainly to liquid phase formation and grain morphology. It was found that the additives such as Al₂O₃ and MgO could modify the microstructure and influence the mechanical behavior.

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1. Introduction

In recent years considerable attention has been devoted to development of nitride and oxynitride bonded SiC refractories.^{1–3} Si₃N₄ bonded SiC is a high quality refractory with interesting mechanical and corrosion resistance properties for industrial applications.⁴ Densification of Si₃N₄ bodies in solid state sintering, due to high directional feature of covalent bonding and its high vapor pressure at high temperatures is very difficult.⁵ It has been claimed that the most effective method for improving the densification of Si₃N₄ bodies, is the addition of metallic oxides.^{6,7} In this method, the formation of sialon and liquid phase modifies the bonding system and enhances the evolution of a desired microstructure.

Microstructural development during the densification assisted by liquid phase is a function of type and amount of additives.^{8,9} In order to optimize the mechanical properties of Si₃N₄ materials, it is necessary to know, the factors that

affect the grain morphology and grain size during sintering process.^{10,11}

Results of the previous papers showed that single and mixed additives such as Al₂O₃, MgO, Y₂O₃, Y₂O₃ + ZrO₂, Al₂O₃ + Y₂O₃, etc., are useful for enhancement of mechanical properties at high temperatures.¹² Although the effect of Al₂O₃ and MgO addition to nitride bonded SiC ceramics have been studied to some extent, the microstructure–properties relationship has not been clarified well. This study aims to report the evolution of the bond system in nitride–silicon aluminium oxynitride, bonded SiC refractories, when Al₂O₃ and MgO are used as additives.

2. Experimental procedures

The alpha SiC powder with particle size below 1.25 mm was supplied by ESK-SiC GmbH. The Si powder was metallurgical grade with average particle size of 15 μm. MgO and Al₂O₃ fine powders were analytical grade. Different amount of oxides were added to a base formula of 75 wt% SiC and

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Table 1
Chemical composition of samples (wt%)

| Samples additives | E | F | G | H | I | J | K | L | M | N |
|--------------------------------|-----|---|---|---|-----|---|---|---|---|---|
| MgO | 0.5 | 1 | 2 | 3 | – | – | – | – | – | – |
| Al ₂ O ₃ | – | – | – | – | 0.5 | 1 | 2 | 3 | 4 | 5 |
| Binder | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |

25 wt% Si as explained in our previous work.¹³ The chemical compositions of samples are shown in Table 1.

Calcium-lignosulphonate was used as a binder and mixing was carried out in a ball mill with polymer lining and zirconia balls. Cylindrical samples were produced by uniaxially pressing in a steel die at 150 MPa. The firing was carried out in a controlled atmosphere furnace at 1450–1600 °C under N₂ flow with soaking time of 5 h.

Density, porosity and cold crushing strength (CCS) were measured according to DIN 51056 and DIN 51067. X-ray phase analysis was performed by using Cu K α radiation in a STOE-STADI-P diffractometer. Polished samples were examined by SEM/EDS Cambridge S-360 system at 10–20 keV. For transmission electron microscopy (TEM), the samples were ground to slices of 1 mm thickness. Three millimetre diameter discs ultrasonically drilled from the slices were mechanically ground and polished to around 80–100 μ m, and then dimpled to 20 μ m center thickness. These dimpled samples were Ar ion milled at 6 keV until perforation, coated with carbon, and examined in a Philips TEM 420 at 120 keV.

3. Results and discussion

3.1. Effect of magnesia

The bulk densities of samples with different amounts of MgO were about 2.57–2.67 g/cm³ depending on firing temperatures. Density is improved with increasing temperature from 1500 to 1600 °C. The density of samples doped with 0.5–3 wt% MgO and fired at 1500 °C for 5 h is almost the same as that of samples without any additive fired at 1550 °C for 5 h. This indicates that the addition of MgO initiates the formation of liquid phase via reaction with silica layer exist-

ing on SiC particles. This was supported by EDS of liquid phase, which revealed Ca, Si and Mg. The ternary diagram of CaO–MgO–SiO₂ shows that the formation of liquid phase can happen at 1400 °C.¹⁴ The presence of CaO in the liquid phase is attributed to the use of calcium-lignosulphonate binder.

Variation of cold crushing strength with different amounts of MgO is shown in Fig. 1. By addition of MgO from 0.5 to 3 wt% the CCS is decreased from 160 MPa to about

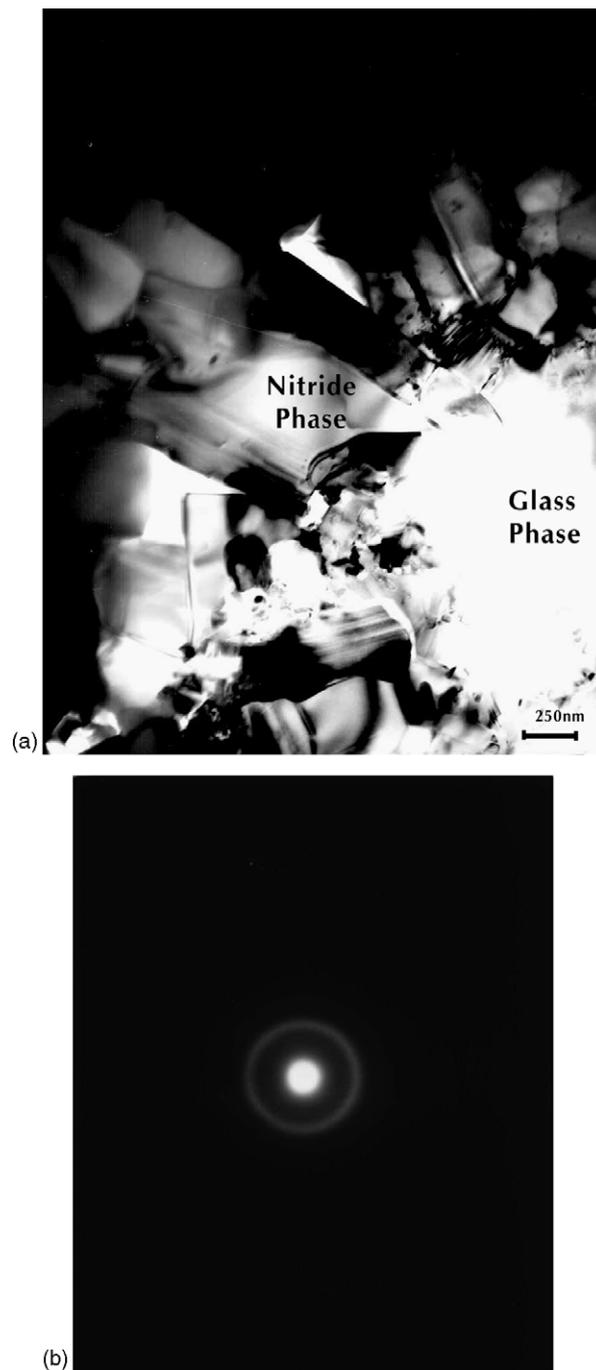


Fig. 2. (a) TEM image of sample G, and (b) diffraction pattern of glassy phases.

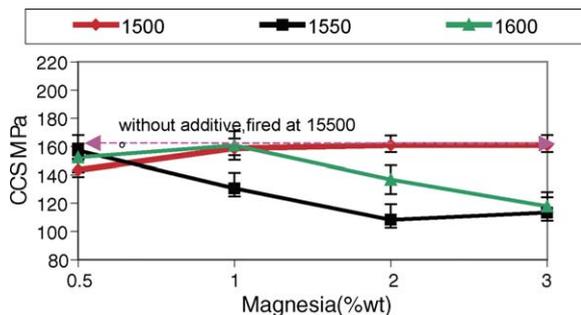


Fig. 1. CCS vs. various amounts of MgO.

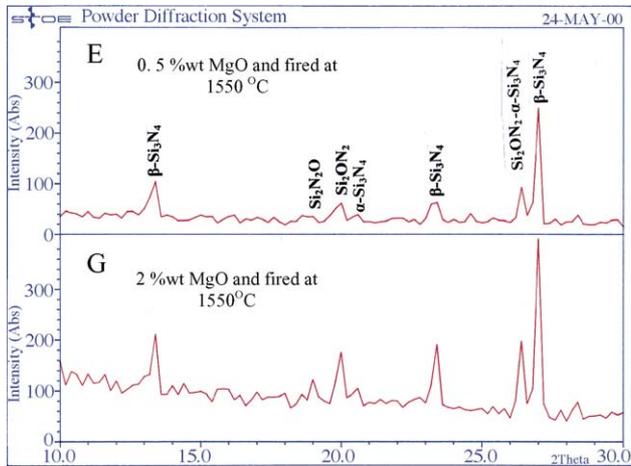


Fig. 3. XRD patterns of samples containing 0.5 and 2 wt% MgO and fired at 1550 °C for 5 h.

120 MPa at 1550 °C. In spite of the variation in CCS values, the density of samples at different temperatures with addition of different amounts of MgO did not show any significant changes. This behavior could be attributed to the fact that the mechanical strength is related to morphology of nitride phases.¹³ Nature of liquid phase affects not only the viscosity but also the morphology of β - Si_3N_4 grains.

The formation of β - Si_3N_4 and liquid phases was confirmed by TEM observations. TEM image (Fig. 2) shows the formation of nitride phases following the solution–diffusion–precipitation (SDP) mechanism. The XRD results of samples containing 0.5 and 2 wt% of MgO are shown in Fig. 3. This as reported before indicates that the liquid phase has a dominant role in the formation of β - Si_3N_4 phase.¹⁵

Fig. 4 shows the SEM micrographs of samples containing 0.5 and 2 wt% MgO and the slight grain size difference of nitride phase due to an increase in MgO amount can be observed. Several microscopical observations clarified that the grain texture mainly influenced in terms of width to length ratio. MgO as a strong modifier reduces viscosity in silicate based glasses.¹⁶ It seems that during reduction of viscosity

by addition of MgO, both nucleation and grain growth are improved. This influence on grain morphology (aspect ratio and grain diameter) is in line with literature.⁹ Probably local super saturation, which is related to kinetic parameters of the liquid phase such as viscosity, affects the morphology of nitride phases and finally influences mechanical properties. In other words the mechanical property variation is more affected by the grain aspect ratio as by the grain size itself. Moreover, the strength decrease also can be attributed to the mismatch expansion nature of liquid and crystal phases. This may initiate the primary cracks in the matrix and decrease the CCS.

3.2. Effect of alumina

The effect of Al_2O_3 additions on density and CCS are shown in Fig. 5. The significant increase in density and cold crushing strength of samples may be observed in this figure. At the first this significant changes due to an increase of only 50 °C may look abnormal. However, this can be explained by referring to ternary diagram of Al_2O_3 – SiO_2 – CaO .¹³ This diagram shows that the formation of liquid phase can happen at 1500 °C and the amount of liquid increases sharply with temperature. The density increase can be attributed to liquid phase formation, which promotes the densification. Also it could be mentioned that by increasing the amount of Al_2O_3 at constant temperatures, the density of samples are not changed significantly.

Another phenomenon in Fig. 5 is the relatively invariable value of density, which shows the significant changes in CCS. The changes in mechanical behavior are influenced not only by β - Si_3N_4 amount and aspect ratio of nitride phase, but also by dissolution of alumina in silicon nitride lattice. At lower amounts of alumina addition, the dissolution of alumina enhances the sintering characteristics. At higher amounts, however, the saturation of alumina leaves some of this material undissolved with a weak bonding. In order to relate the mechanical behavior dependence to microstructure, XRD, SEM and TEM were employed. Based on XRD patterns, by addition of Al_2O_3 up to 3 wt% the β '- Si_3N_4 sialon phase is increased that leads to improve the mechanical properties. Fig. 6 illustrates the phase variation in samples

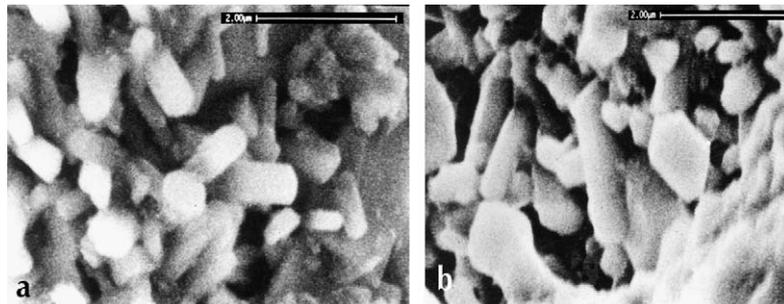


Fig. 4. SEM micrographs of samples containing (a) 0.5 wt% MgO and (b) 2 wt% MgO.

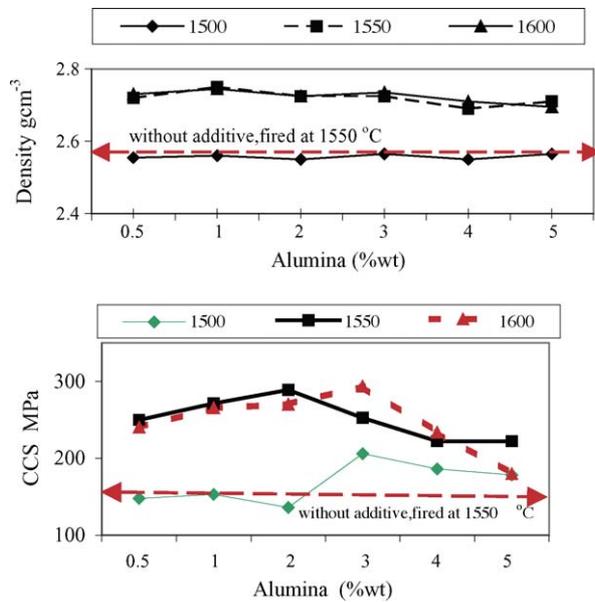


Fig. 5. Density and CCS vs. various percent of Al_2O_3 additive, (a) density, and (b) CCS.

containing 0.5–5 wt% of alumina. The increase of β' - Si_3N_4 sialon is clearly accompanied by an improvement in mechanical behavior. The reaction between Al_2O_3 and SiO_2 (as a layer on SiC) enhances the formation of liquid phase and β' - Si_3N_4 sialon from SDP mechanism. The Ca introduced by lignosulphonate binder also can play a role in modifying the amount and viscosity of liquid phase. The SEM illustration in Fig. 7 shows that in the sample containing 0.5 wt% alumina, the α - Si_3N_4 is the dominant phase, whereas in sample containing 3 wt% alumina the β' - Si_3N_4 sialon is the main phase. Samples containing 3 wt% alumina did not show the special change to compare with sample 5 wt% alumina.

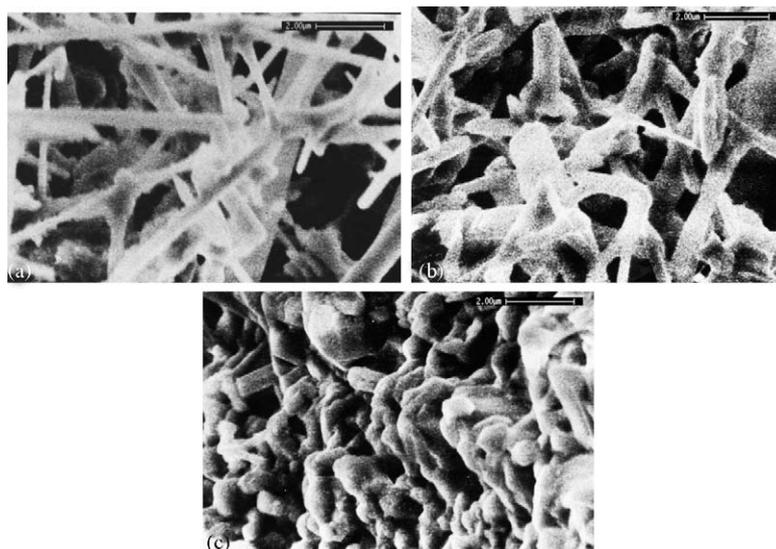


Fig. 7. SEM micrographs of alumina doped samples, (a) 0.5 wt% Al_2O_3 , (b) 3 wt% Al_2O_3 and (c) 5 wt% Al_2O_3 .

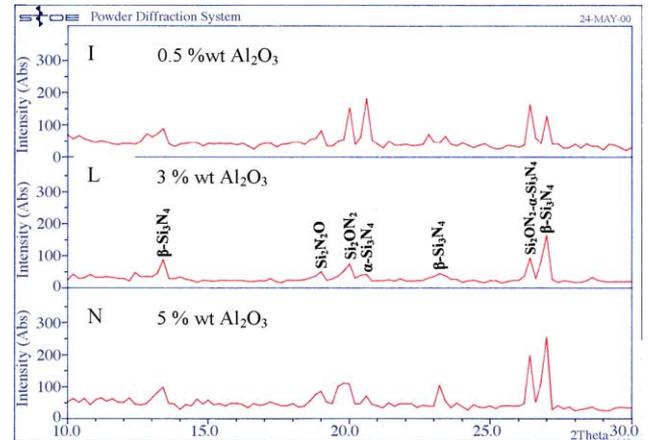


Fig. 6. XRD patterns of alumina doped samples.

This finding is supported by XRD analysis already explained above. However, in order to justify strongly the influence on mechanical properties an instrument such as TEM is required.

Bright field image (BF) and diffraction pattern (DP) of samples are shown in Fig. 8(a) and (b). In this figure the nitride bond and liquid phase trapped between the grains can be observed clearly. The EDS analysis clarifies the solution of Al_2O_3 in Si_3N_4 matrix. By doping of Si_3N_4 with Al and O, the Si_3N_4 lattice parameters are increased. Therefore the diffusion of Si and N is enhanced that leads to better densification. SEM showed small white unreacted particles dispersed in the matrix. Microanalysis revealed that particles contained aluminium and silicon. Either of these particles can naturally cause a decrease in mechanical strength.

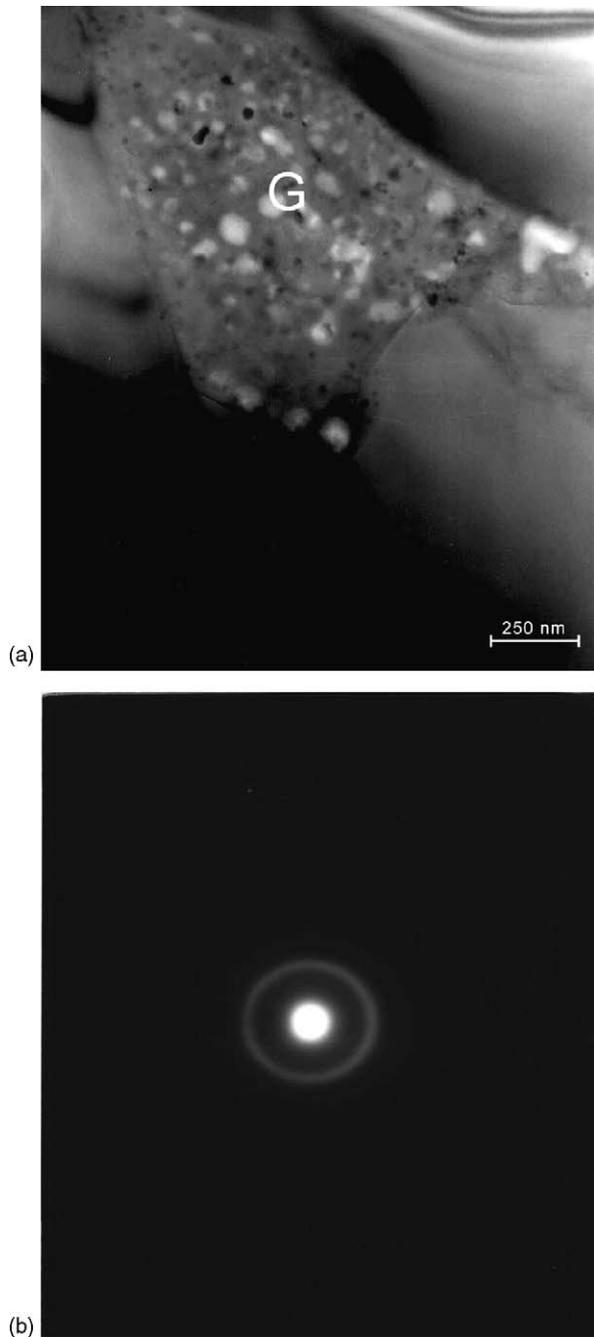


Fig. 8. (a) TEM bright field micrograph of sample L, (b) diffraction pattern of point G.

4. Conclusions

The addition of MgO and Al₂O₃ to nitride-bonded SiC refractories which leads to variation in mechanical properties can be explained by different microstructures changes:

1. In samples containing magnesia as additive the mechanical variation is more affected by the grain aspect ratio than the grain size itself.
2. The strength decrease can be attributed to the mismatch of expansion coefficients of liquid and crystal phase as

well as changes on aspect ratio of needlelike nitride phase.

3. The variation in mechanical properties are influenced not only by β -Si₃N₄ amount and aspect ratio of nitride phase, but also by dissolution of alumina in Si₃N₄ lattice (formation of β -sialon).
4. The low cold crushing strength in high alumina doped samples is attributed to undissolved Al₂O₃ which causes a weak bond.

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