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A new sintering additive for silicon carbide ceramic

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Abstract

Silicon carbide (SiC) ceramic with nanoscale silicon carbide powder and oxide ($MgO+Al_2O_3+Y_2O_3$) or nitrate salt [$Mg(NO_3)_2+Al(NO_3)_3+Y(NO_3)_3$] additives was hot-pressed at 1800 °C, 25 MPa, for 30 min. All the samples had fine, equiaxed microstructures with an average grain size less than 1 μm. The addition of nanoscale SiC did not effectively improve the relative density. Whether nano-SiC was added or not, the samples with nitrate salt additives had a higher relative density than their counterparts with oxide additives, and the maximum values were as high as 98.1 and 97.7%, respectively. Crystalline YAG phase was detected by XRD only in samples with nitrate salt additives, and the major phases in the oxide additive samples were the same 3C and 4H polytypes as those in the starting powders. Compared with the previous study, the elemental distribution of Y, Al, and Mg was more homogeneous in the oxide additive samples.

Keywords: A. Hot pressing; D. Silicon carbide; Sintering additives

1. Introduction

Silicon carbide (SiC) is a promising material for high temperature engineering applications, however, it is difficult to densify without additives because of the covalent nature of Si–C bonding and low self-diffusion coefficient [1]. Boron, aluminum, carbon, or their compounds have been successfully used as sintering aids to fabricate SiC ceramics at about 2000 °C [2]. Liquid phase sintering with the addition of MgO and/or Al_2O_3 and/or Y_2O_3 has been also investigated at 1850–2000 °C [3–7]. But the additives used to enhance processing invariably become ‘‘weak’’ secondary phase in the final ceramic [8–10], which usually lower its mechanical properties at high temperature. This detrimental effect infers that the smallest fraction of additives is desirable. In addition, the effectiveness of the additives greatly depends on the homogeneity of their distribution [11].

Due to lower sintering temperature than normal powders, ultrafine powders have been used as sintering agents [12]. Also, when adopted as sintering additives in silicon nitride (Si_3N_4) ceramic, nitrate salts are more homogenously distributed than their oxide counterparts during the ball-milling process [13,14]. The main purpose of the present study is to combine the advantages of the above-mentioned additives. We blend nanoscale and submicron SiC powders to improve sinterability, use nitrate salts instead of oxide as sintering aids, and try to minimize the amount of additives to fabricate silicon carbide ceramic.

2. Experimental procedure

Commercially available sub-micron powders of β-SiC (Central Iron and Steel Research Institute, Beijing, China) with an average particle size of 0.5 μm and 70 nm nano-SiC (East Nanometer Materials Co., Ltd, Shijiazhuang, China) were used. Nitrate salts $Mg(NO_3)_2 6H_2O$ (99.0% purity, Beijing Chemical Plant, China), $Al(NO_3)_3 9H_2O$ (99.0% purity, Beijing Chemical Plant, China) and $Y(NO_3)_3 6H_2O$ (⩾99% purity, Special Type Chemical Reagent Development Co. of North China) were adopted as sintering additives. To compare the effects of nitrate and oxide additives, MgO (98.0% purity, Minfeng Reagent Plant of Wuxi, China),

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Al_2O_3 (Beijing Construction Material Research Institute, China) and Y_2O_3 (99.9% purity) were also used as sintering aids. The composition of different samples was referred to Table 1. The amounts of nitrates were calculated based on their oxide forms. All the individual batches were milled in ethanol for 24 h using Si_3N_4 balls and then dried in air on a hot plate. When nitrate additives were used, the solutions were added to the bottles for ball milling after the nitrate salts had been dissolved in ethanol. The ball-milled and dried powders with nitrate sintering additives were calcined at 500 °C for 2 h in a nitrogen-gas atmosphere to decompose the nitrates. Hot-press sintering was performed on an FVHP-R-50 FRET-100 furnace (Fuji Dempa Kogyo Co. Ltd., Japan) at 1800 °C, 25 MPa, for 30 min in an argon atmosphere.

The density of the specimen was determined by the Archimedes method. The theoretical density was calculated according to the rule of mixtures. The microstructure was observed by scanning electron microscopy (SEM) system (Model X-650, Hitachi). Before SEM observation, the specimen was polished, and then chemical-etched (boiling Murakami reagent) for 30 min. Crystalline phases were determined by X-ray diffraction measurements (D/max$_1$-rB, Japan) using CuK_α radiation. The distribution homogeneity of elemental yttrium, aluminum, and magnesium in the sintered samples was examined by electron microprobe (Jeol Superprobe 733, Japan).

3. Results and discussion

3.1. Relative density and microstructure

Figs. 1 and 2 show the relative density of the sintered samples. All the samples with oxide additives have a value above 95.8%, and obviously, the addition of nano-SiC particles decreases the relative density, which is true both in the samples with oxide additives and the ones with nitrate salt additives. As the content of nano-SiC increases, the relative density slightly increases, but it is still lower than the samples without nano-SiC particles. The result is consistent with findings reported by Sciti [15]. The decrease of relative density after nano-SiC powder addition has probably resulted from the larger amount of silica coming from nano-SiC powder, which increases the amount of liquid phase during hot-pressing. More liquid phase will aggravate the volatilization problem and result large size grain boundary phase pockets in the final ceramic.

In the samples with nitrate salt additives, the relative density increases almost linearly with the increasing amount of nitrate salts. Fig. 3 compares the effect on

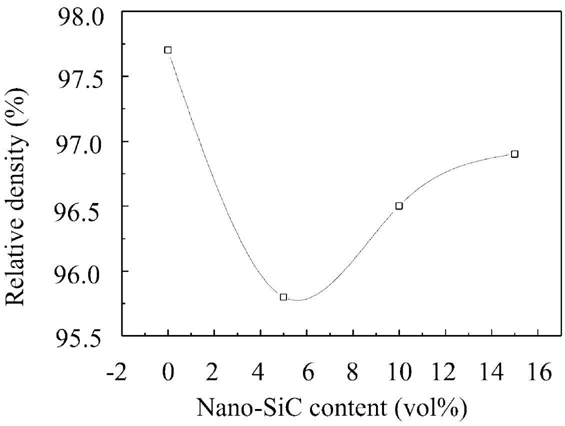

Fig. 1. The relative density of the samples with 9 wt.% (MgO +

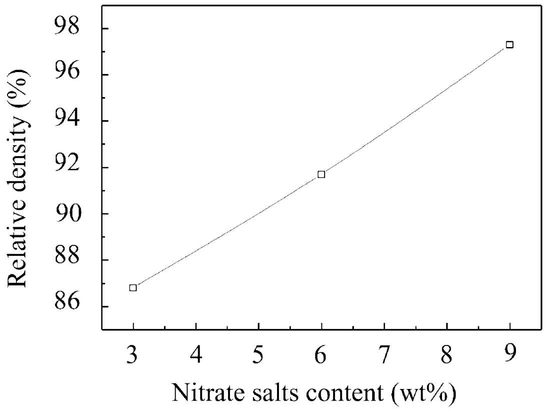

Fig. 2. The relative density of the [$Mg(NO_3)_2 + Al(NO_3)_3 + Y(NO_3)_3$]

Table 1
Starting composition of SiC + additives

Sample	Composition	Amount of additives (wt.%)
S9O	SiC + oxide additives	9
S5S9O	SiC + 5 vol.% nano-SiC + oxide additives	9
S10S9O	SiC + 10 vol.% nano-SiC + oxide additives	9
S15S9O	SiC + 15 vol.% nano-SiC + oxide additives	9
S9N	SiC + nitrate additives	9
S10S9N	SiC + 10 vol.% nano-SiC + nitrate additives	9
S10S6N	SiC + 10 vol.% nano-SiC + nitrate additives	6
S10S3N	SiC + 10 vol.% nano-SiC + nitrate additives	3

The molar ratio of the additive composition was fixed at $MgO:Al_2O_3:Y_2O_3 = 67:16:17$.

relative density of oxide sintering aids with that of nitrate salts. It shows that the samples with nitrate salt additives have a higher relative density. Note that the sample with only 3 wt.% sintering additives, hot-press sintered at 1800 °C for just 30 minutes has a relative density of as high as 86.8%, which is difficult to achieve in the sintering of silicon carbide ceramic.

Figs. 4 and 5 present the secondary electron SEM images of the samples. Note that all the samples have fine, equiaxed microstructures with an average grain size less than 1 μm. This is due to the low sintering temperature, lower soaking time, and the addition of nano-SiC particles. Except for S10S6N and S10S3N, which are less densified and have more residual pores, all the samples have a relatively homogeneous microstructure without abnormal grains. The microstructure of the samples is consistent with the relative density data mentioned previously.

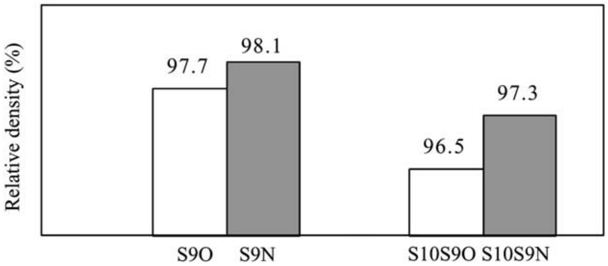

Fig. 3. The relative density comparison between the samples with oxide and nitrate salt additives.

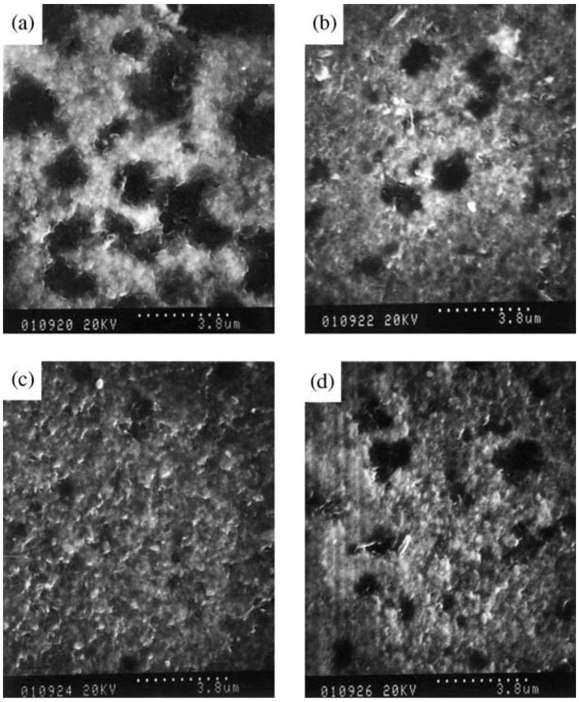

Fig. 4. Secondary electron SEM images of the samples with oxide additives (a) S9O, (b) S5S9O, (c) S10S9O, (d) S15S9O.

3.2. XRD analysis

Figs. 6 and 7 demonstrate the phase analysis results by XRD. The major phases in the oxide additive samples are 3C and 4H polytypes, which are present in the starting SiC powders, therefore there is no new phase produced during the hot-pressing process. And as the content of the additives is small, XRD cannot detect them. In the nitrate salt additive samples S9N and S10S9N, XRD detects the diffraction peaks of YAG ($Al_5Y_3O_{12}$), which is the lowest eutectic phase between Al_2O_3 and Y_2O_3 and beneficial to the fracture toughness of liquid phase sintered silicon carbide (LPSSC) ceramic [16,17]. Because of still lower additives content in

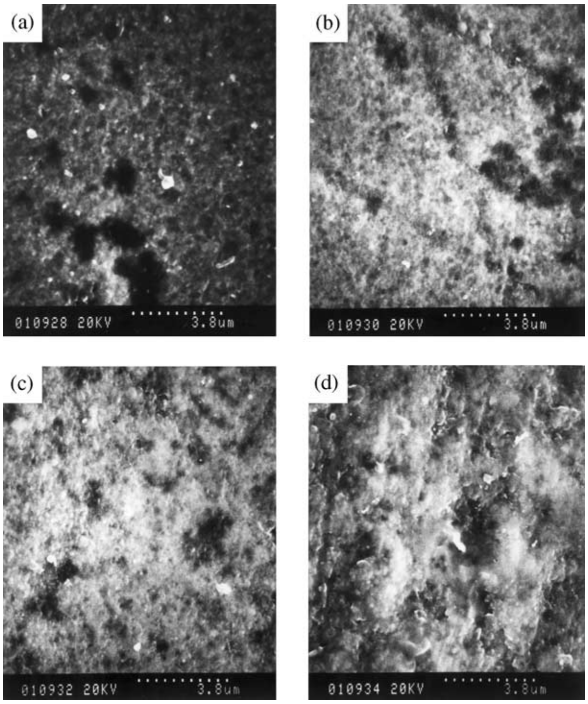

Fig. 5. Secondary electron SEM images of the samples with nitrate additives (a) S9N, (b) S10S9N, (c) S10S6N, (d) S10S3N.

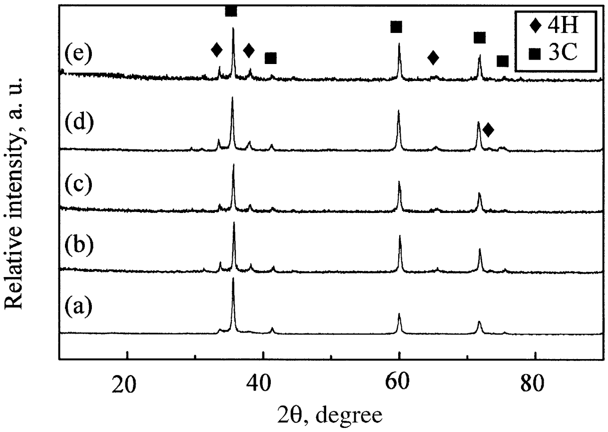

Fig. 6. XRD analysis of the samples with oxide additives: (a) starting SiC powder, (b) S9O, (c) S5S9O, (d) S10S9O, (e) S15S9O.

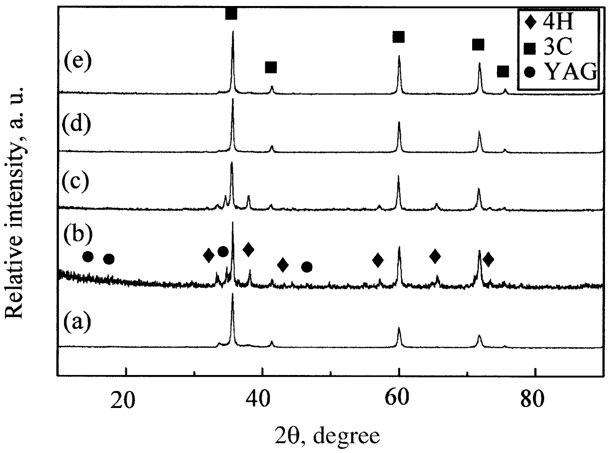

Fig. 7. XRD analysis of the samples with nitrate additives (a) starting SiC powder, (b) S9N, (c) S10S9N, (d) S10S6N (e) S10S3N.

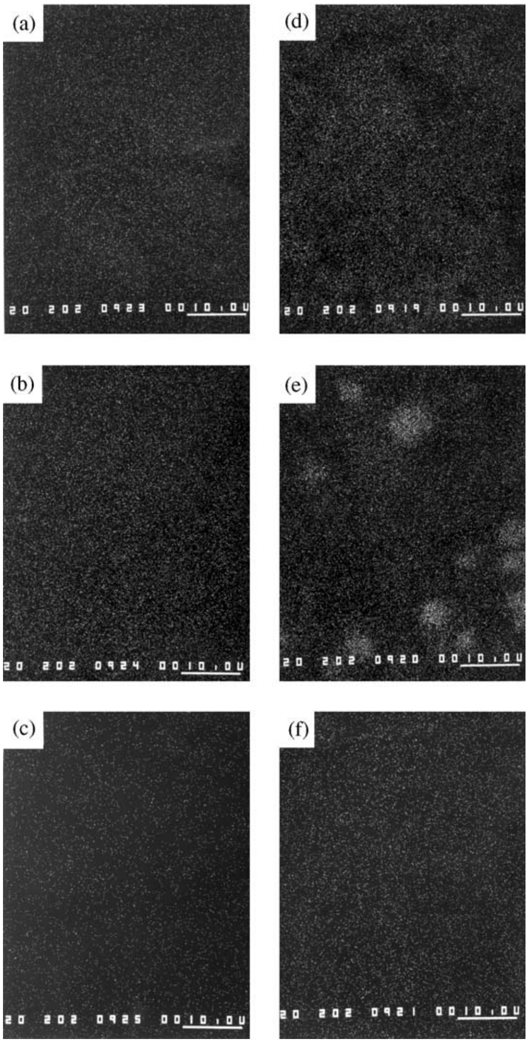

Fig. 8. Elemental distribution mapping in the sintered samples: (a) Y in S10S9O, (b) Al in S10S9O, (c) Mg in S10S9O, (d) Y in S10S9N, (e) Al in S10S9N, (f) Mg in S10S9N.

S10S6N and S10S3N samples, the detected diffraction peaks of these samples are the same as the starting SiC powders.

3.3. Elemental distribution analysis

Fig. 8 shows the elemental distribution mapping in the samples S10S9O and S10S9N. Contrary to the results presented in Ref. [14], the distribution of elemental yttrium, aluminum and magnesium is more homogeneous in the samples with oxide additives. The difference may be caused by the addition of nano-SiC particles. However, the authors also found many aggregates of the additives in the specimen of S9N. The only reason that can account for the phenomenon lies in the hot-pressing process. The detailed reasons for this difference need further study.

4. Conclusion

Silicon carbide ceramic fabricated by hot-pressing using nanoscale SiC powder and nitrate salts as sintering additives had a fine, equiaxed microstructures with an average grain size less than 1 μm. The sintered samples with nitrate salt additives had higher relative density than the ones with oxide additives. The highest relative densities in the nitrate salt and oxide additive samples are 98.1 and 97.7%, respectively. XRD detected YAG phase, which is beneficial to the fracture toughness of the ceramic, only in the nitrate salt additive samples. The electron probe analysis indicated that the elemental distribution of Y, Al, and Mg was more homogeneous in sintered samples with oxide additives.

References

[1] S.J. Guo, Theory of Powder Metallurgy, Metallurgical Industry Press, 1998, pp. 288–291 (in Chinese).

[2] S. Prochazka, The role of boron and carbon in the sintering of silicon carbide, in: P. Popper (Ed.), Special Ceramics, vol. 6, The British Ceramic Research Association, 1975, pp. 171–181.

[3] M. Omori, H. Takei, Pressureless sintering of SiC, J. Am. Ceram. Soc. 65 (6) (1982) C–92.

[4] M.A. Mulla, V.D. Krstic, Low-temperature pressureless sintering of β-silicon carbide with aluminum oxide and yttrium oxide additions, Am. Ceram. Soc. Bull. 70 (1991) 439–443.

[5] N.P. Padture, In situ-toughened silicon carbide, J. Am. Ceram. Soc. 77 (2) (1994) 519–523.

[6] S.K. Lee, Y.C. Kim, C.H. Kim, Microstructural development and mechanical properties of pressureless-sintered SiC with plate-like grains using Al_2O_3-Y_2O_3 additives, J. Mater. Sci. 29 (1994) 5321.

[7] D. Foster, D.P. Thompson, The use of MgO as a densification aid for α-SiC, J. Eur. Ceram. Soc. 19 (1999) 2823–2831.

[8] D.H. Kim, C.H. Kim, Toughening behavior of silicon carbide with additions of yttria and alumina, J. Am. Ceram. Soc. 73 (1990) 1431–1434.

[9] M.A. Mulla, V.D. Krstic, Mechanical properties of β-SiC pressureless sintered with Al_2O_3 additions, Acta Mettall. Mater. 42 (1) (1994) 303–308.

[10] N.P. Padture, B.R. Lawn, Toughness properties of a silicon carbide with an in situ induced heterogeneous grain structure, J. Am. Ceram. Soc. 77 (1994) 2518–2522.

[11] E. Lidén, E. Carlström, L. Eklund, B. Nyberg, R. Carlsson, Homogeneous distribution of sintering additives in liquid-phase sintered silicon carbide, J. Am. Ceram. Soc. 78 (7) (1995) 1761–1768.

[12] R. Vaβen, A. Kaiser, J. Förster, H.P. Buchkremer, D. Stöver, Densification of ultrafine SiC powders, J. Mater. Sci. 31 (1996) 3623–3637.

[13] J.-Y. Kim, T. Iseki, T. Yano, Pressureless sintering of dense Si_3N_4 and Si_3N_4/SiC composites with nitrate additives, J. Am. Ceram. Soc. 79 (10) (1996) 2744–2746.

[14] D.-C. Park, T. Yano, T. Iseki, K. Urabe, Effect of nitrate salts as sintering additives during the ball-milling process of silicon nitride powders, J. Am. Ceram. Soc. 83 (12) (2000) 2967–2973.

[15] D. Sciti, A. Bellosi, Effect of additives on densification, microstructure and properties of liquid-phase sintered silicon carbide, J. Mater. Sci. 35 (2000) 3849–3855.

[16] J.H. She, K. Ueno, Densification behavior and mechanical properties of pressureless-sintered silicon carbide ceramics with alumina and yttria additions, Mater. Chem. Phys. 59 (1999) 139–142.

[17] G. Magnani, G.L. Minoccari, L. Pilotti, Flexure strength and toughness of liquid phase sintered silicon carbide, Ceram. Int. 26 (2000) 495–500.