[Article ID] 1003 - 6326(2000)04 - 0516 - 04

Preparation and mechanical properties of Si_2N_2O ceramics①

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[Abstract] Si_2N_2O ceramics was fabricated from pre-synthesized Si_2N_2O powder by the hot-pressed sintering method. The results indicated that the highest relative density and hardness(HRA) of the sample are almost 100 % and 93, respectively. Moreover, effects of some experimental parameters (such as the amount of sintering aid agent Y_2O_3, sintering time and temperature) on the density and microstructure of ceramics were investigated, and effects of the density and microstructure on some mechanical properties(HRA, σ_f and K_{IC}) were also discussed.

[Key words] silicon oxynitride; preparation; ceramics; properties
[CLC number] TQ174.75 [Document code] A

1 INTRODUCTION

Silicon oxynitride (Si_2N_2O) ceramics should be regarded as a fine refractory because of its excellent resistance to oxidation and erosion of melt silica and nonferrous metals. In addition, it has been recognized as a promising engineering material because of its good mechanical properties similar to Si_3N_4 and SiC ceramics[1~4].

Silicon oxynitride ceramics may be prepared in two different ways. One is to sinter the mixture powder of Si_3N_4 and SiO_2 according to the following reaction:

$$Si_3N_4 + SiO_2 = 2Si_2N_2O \quad (1)$$

Another is to sinter the pre-synthesized Si_2N_2O powder directly. It seems that the latter method is more advantageous because it allows more suitable processing. However, reports and papers about Si_2N_2O ceramics are very rare up to today in China, in fact, and there are no more in other countries. Especially, any references about preparing Si_2N_2O ceramics by the second method are not found. This paper aims to prepare Si_2N_2O ceramics by using Si_2N_2O powder pre-synthesized, and study the effects of experimental parameters on the mechanical properties of the ceramics.

2 EXPERIMENTAL

2.1 Raw materials

Si_2N_2O powder (The mass fractions of Si_2N_2O and cristobalite are about 93 % and 7 %, respectively, mean size 0.88 μm and synthesizing method refers to Refs.[5,6]); N_2(high purity); Y_2O_3(A.R); absolute alcohol (industrial purity); Si_3N_4 powder (α-Si_3N_4 > 88 %, N > 38 %).

2.2 Procedure

Since there was about 7 % cristobalite in the raw Si_2N_2O powder, a moderate amount of Si_3N_4 powder was added into the mixture in order to reduce the quantity of residual SiO_2 in the ceramics which will be fabricated in further experiments. This was based on reaction (1) during sintering process in which SiO_2 and Si_3N_4 would react and form Si_2N_2O.

The mixture powder of raw Si_2N_2O, Si_3N_4 and Y_2O_3 was milled with absolute alcohol and Al_2O_3 balls for 4 h in a plastic jar, then the mixture was dried. The dried mixture powder was sintered under 30 MPa pressure in N_2 atmosphere. By altering sintering time or(and) temperature, samples with different properties were obtained.

The bulk density ρ_r and apparent porosity P_0 of the sintered body was measured according to the Archimedes principle, then the relative density γ was calculated through the following formula:

$$\gamma = \frac{\rho_r}{\rho_h} \quad (2)$$

Where ρ_h is the theoretical density of the Si_2N_2O ceramic sample, and it is obtained through:

$$\rho_h = \sum w_i \rho \quad (3)$$

where w_i is the mass percentage of i composition in Si_2N_2O ceramic sample, and ρ is the theoretical density.

The fracture toughness K_{IC} and flexural strength σ_f were measured by MTS Ceramics Mechanics Properties System (MTS8100, America), and all the test bars were polished and cut using 220 SiC milling-pa-

① [Foundation item] Project (29401005) supported by the National Natural Science Foundation of China
[Received date] 1999 - 06 - 16; [Accepted date] 1999 - 09 - 01

per. Then K_{IC} was assessed by using the single edge notched beam (SENB) technique in three point bend (test bars size 2.5 mm × 5.0 mm × 30 mm; span length 20 mm; crosshead speed 0.05 mm/min), and σ_f was assessed from three point bend test, using a crosshead speed of 0.5 mm/min and a span length of 25 mm (test bars size: 3 mm × 4 mm × 30 mm). Hardness (HRA) was determined by a digital hardometer (HRS-150, Shandong, China). Micrograph of the fracture face was observed using a scanning electron microscope (SEM, SX-40, Akashi Seisakusho Ltd, Japan).

3 RESULTS AND DISCUSSION

3.1 Results

The densities and mechanical properties of ceramics samples and some experimental parameters are listed in Table 1. Fig.1 illustrates SEM micrographs of the fracture surfaces of samples.

Table 1 Condition and results on preparation of Si_2N_2O ceramics

Sample No.	$w(Y_2O_3)$	θ/℃	t/h	γ/%	P_0/%	HRA	σ_f/MPa	K_{IC}/(MPa·$m^{1/2}$)	Microstructure
1	0	1650	1.0	75	25.3	60.8	158	2.32	Fig.1(a)
2	3.0	1650	1.0	99	0.4	92.7	485	3.34	Fig.1(b)
3	5.0	1650	1.0	98	0.5	92.1	411	3.98	Fig.1(c)
4	5.0	1550	1.0	81	20.0	64.5	180	2.65	Fig.1(d)
5	5.0	1600	1.0	95	1.7	88.5	404	3.68	Fig.1(e)
6	5.0	1650	0.5	94	1.8	86.8	370	3.30	Fig.1(f)
7	5.0	1650	1.5	100	0.2	93.0	407	2.97	Fig.1(g)

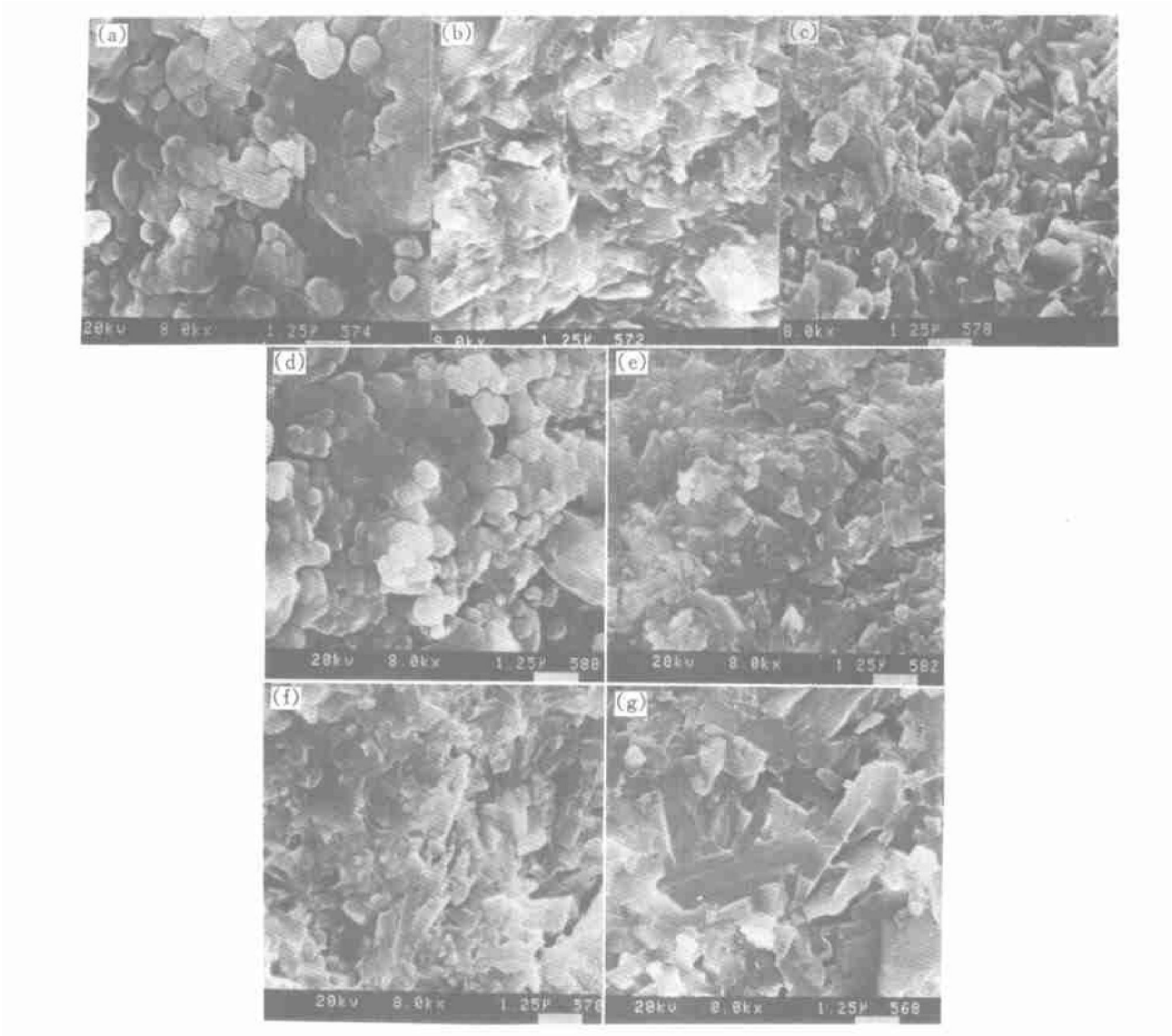

Fig.1 SEM fractographs of Si_2N_2O ceramic samples

(a) —Sample 1; (b) —Sample 2; (c) —Sample 3; (d) —Sample 4; (e) —Sample 5; (f) —Sample 6; (g) —Sample 7

3.2 Effects of experimental parameters on density and microstructure of ceramic samples

It is showed that the densities and micrographs of the hot-pressed Si_2N_2O ceramic samples were affected by the addition amount of Y_2O_3, the sintering time and temperature.

3.2.1 Effects of amount of Y_2O_3 as sintering aid agent

By comparison the experimental parameters with the results of samples 1, 2 and 3 in Table 1, it can be discovered that when 3% Y_2O_3 was added into the raw mixture powder, the relative density and apparent porosity of the sintered sample reached the max and min, respectively.

Theoretically, the eutectic between Y_2O_3 and SiO_2 is 1 650 ℃, but it would be below 1 650 ℃ because of the existence of other compositions. The fact that Y_2O_3 and SiO_2 would form liquid phase under sintering temperature would facilitate the densification of bulk bodies. At the same time, Y_2O_3 and SiO_2 would form Si_2N_2O according to reaction (1), and during the hot-pressed sintering process they would further form a fine refractory $Si_3N_4 \cdot Y_2O_3$[7]. Therefore, the content of $Si_3N_4 \cdot Y_2O_3$ in the grain boundaries would increase with the increase of the Y_2O_3 content in the raw mixture powder. But there is a subtle difference between the expansion coefficient of the Si_2N_2O matrix and that of the grain phase $Si_3N_4 \cdot Y_2O_3$, and the subtle difference would result in some microcracks occurring in the sintered materials.

Fig.1(a), (b) and (c) are micrographs of the fracture surfaces of samples 1, 2 and 3, respectively. Comparing Figs.1(a), (b), (c), it is observed that grains stacked closer and closer, which suggests that these samples became denser. Moreover, grains gradually became elongated from spherical, which suggests they grew finer.

3.2.2 Effects of sintering temperature

The data of samples 4, 5 and 3 in Table 1 indicate that the relative densities of samples gradually increased while their apparent porosity gradually decreased with increasing the sintering temperature. It was because elevated temperature could promote the mass transfer during the sintering process, and result in further densification of the samples.

In addition, Figs.1(d) and (e) are the micrographs of the fracture surfaces of sample 4 and 5, respectively, which further illustrate that grains grew finer, and stacked closer.

3.2.3 Effects of sintering time

The data of samples 6, 2 and 7 in Table 1 indicate that the relative densities of samples gradually increased while their apparent porosity gradually decreased with increasing the sintering time. Because elongating the sintering time would make the plastic flow and diffusion easier and quicker in sample bodies when the sintering process was in its middle or(and) late period. However, to quicken plastic flow and diffusion would make the densification of bodies easier, that is, make the densities of the ceramic samples higher.

In addition, Figs.1(f), (b) and (g) are the micrographs of the fracture surfaces of sample 6, 2 and 7, respectively, which also further illustrated that grains grew finer, and stacked closer.

3.3 Effects of experimental parameters on mechanical properties

The data in Table 1 indicate that mechanical properties (HRA, K_{IC} and σ_f) of ceramic samples changed with the change of experimental parameters. Nevertheless, the experimental parameters affected their mechanical properties by affecting the densities and microstructures of the samples. For convenience of the discussion, Table 1 has been transformed into Fig.2.

3.3.1 Hardness

Curve 3 in Fig.2 clearly shows that the hardness of samples accordingly increased with their relative densities, which denotes an ability that a solid resists to be made a dent in its surface. It is mainly relative to the bind strength of the solid[8]. So the denser the material is, the stronger its resistance ability is, that is, the higher its hardness is.

3.3.2 Flexural strength

From curve 2 in Fig.2, it can be observed that the flexural strength increased as the relative density increased before ceramic samples were completely dense, and when γ reached to 99%, σ_f reached its' max.

The interrelation between the flexural strength and apparent porosity of ceramic materials can be approximately expressed as follows[9]:

$$\sigma_f = \sigma_0 e^{-bp} \quad (4)$$

where p is the apparent porosity, b is a constant, and σ_0 is the flexural strength when $p = 0$.

Curve 4 in Fig.2 clearly illustrate that the apparent porosity p_0 gradually decreased with increasing γ. However, curve 1 (except for $\gamma = 100\%$) in Fig.2 shows that the changing tendency of σ_f with γ is contrary to that of P_0 with γ, that is, σ_f may gradually increased with decreasing P_0.

However, when the density of samples is almost the theoretical value, effects of the size and morphology of grains on σ_f must be counted. And between σ_f of fragile materials like ceramics and their grain size exists the following approximate equation[9]:

$$\sigma_f = kd^{-1/2} \quad (5)$$

where k is a constant, and d is the mean grain size.

According to Eqn.(5), σ_f may decrease with increasing the mean grain size. Comparing the micro-

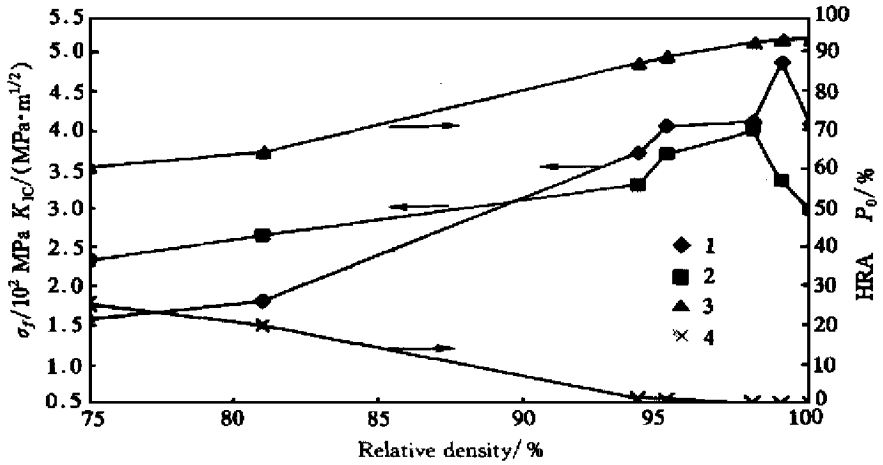

Fig.2 Relationships between density and some properties of Si_2N_2O ceramic sample
1 — σ_f; 2 — K_{IC}; 3 — HRA; 4 — P_0

graph of the fracture surface of sample 2 with that of sample 7 (Fig.1(b) and (g)), it can be observed that the latter grains were apparently bigger than the former ones. At the same time, both of their densities were almost the theoretical values, so the latter σ_f should be lower than the former one. Investigating the relevant data in Table 1 and micrographs in Fig. 2, it was thought that the experimental results were in accordance with the mentioned-above analysis.

3.3.3 Fracture toughness

When the material density is near to the theoretical value, K_{IC} is similar to σ_f, that is, K_{IC} would be primarily affected by the material microstructure, and the interrelation between σ_f and K_{IC} can be approximate expressed as follows[9]:

$$\sigma_f = \frac{1}{\pi(1-\upsilon^2)}\left(\frac{K_{IC}}{\sqrt{c}}\right) \quad (6)$$

where υ is Poisson ratio, c is the half-length of cracks.

σ_f is affected by c and the shape of cracks, but K_{IC} is not affected by c[9,10]. Moreover, as the material density is approaching the theoretical value, the inner microcracks would relax the stress concentration on the tip of the main crack, which would hinder the propagation of the crack, that is, K_{IC} would increase. In fact, the analysis above has pointed out that excessive of Y_2O_3 in the raw mixture powder would result in cracks occurring in the material. Therefore, K_{IC} of sample 3 was bigger than that of sample 2.

4 CONCLUSIONS

1) To add Y_2O_3 as sintering aid agent is benificial to densifying Si_2N_2O ceramics.

2) To elevate sintering temperature or(and) elongate sintering time can densify Si_2N_2O samples, lower their apparent porosity, and promote Si_2N_2O grains growing.

3) The denser the Si_2N_2O samples are, the bigger their HRA, σ_f and K_{IC} are. However, when the density is near the theoretical value, σ_f and K_{IC} will be mainly affected by the microstructure and the grain size of the samples.

[REFERENCES]

[1] Boch P and Glandus J C. Elastic properties of silicon oxynitride [J]. J Mat Sci, 1979, 14: 379 - 383.

[2] Washburn Malcom E. Silicon oxynitride refractories [J]. J Am Ceram Soc, 1967, 46(7): 667 - 671.

[3] Bergman B and Huang H P. The influence of different oxides on the formation of Si_2N_2O from SiO_2 and Si_3N_4 [J]. J Europ Ceram Soc, 1990, 6: 3 - 8.

[4] O' Meara J C, Sjöberg J, Doulop G, et al. Oxidation of pressless sintering Si_2N_2O materials [J]. J Europ Ceram Soc, 1991, 7: 369 - 378.

[5] YAN Yu-hua, OUYANG Shi-xu and WANG Si-qing, et al. Preparation of Si_2N_2O powder from natural quartz powder [J]. The Chinese Journal of Nonferrous Metals, (in Chinese), 1997, 7(4): 84 - 87.

[6] WANG Si-qing and YAN Yu-hua. Influence of silicon source on synthesis of Si_2N_2O powder [J]. Journal of Ceramics, 1997, 18(3): 154 - 157.

[7] YIN Sheng. Advanced Ceramics and Their Applications [M]. Beijng: Beijing University of Technology Press, 1990: 154.

[8] JIN Zong-zhe and BAO Yi-li. Assessments and Designs of Mechanical Properties of Fragile Materials [M]. Beijing: Chinese Railway Press, 1996.

[9] ZHANG Qing-chun. Mechanical Properties of Ceramics [M]. Beijing: Beijing Science Press, 1987. 91 - 147.

[10] WANG Lin-sen. Special Ceramics [M]. Changsha: Central South University of Technology Press, 1998. 128.

(Edited by HUANG Jin-song)