Resistance of Si_2N_2O ceramics to oxidation and erosion of molten silica [①]

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Abstract : Si_2N_2O ceramics was fabricated from powder by hot-pressing in N_2 atmosphere . The resistance of the ceramic sample to oxidation and erosion of molten silica was investigated . The bulk density and open porosity of the ceramic sample were measured according to the Archimedes principle in water . Then fracture surface of the sintered body was observed by SE M . The results and analysis indicate that the resistance of Si_2N_2O ceramics to oxidation and erosion of molten silica increases when its density increases and/ or its open porosity decreases . Moreover , they also reveal that the oxidation process is an unsteady dispersing process with oxygen as the constant source , and the resistance to erosion of molten silica related to the quantity of grain boundary in unit surface area . The lowest mass gain is 2 .4 g/ m^2 after oxidizing at 1 000 ℃ for 100 h in air , while the lowest mass loss is 2 .9 g/ m^2 after 40 h erosion in molten silica .

Key words : silicon oxynitride ; ceramics ; chemical stability   **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 molten 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 in principle 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 :

$$Si_3N_4 + SiO_2 = 2Si_2N_2O \qquad (1)$$
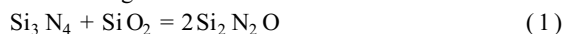
Another is to sinter the pre-synthesized Si_2N_2O powder directly . It seems that the latter method is more advantageous because it allows more suitable processing . However , up to today , reports and papers about Si_2N_2O ceramics have been rare in China , no more then in other countries . Especially , we have not found any literature about preparing Si_2N_2O ceramics via the second method . This paper aims to inquire the resistance of Si_2N_2O ceramics to oxidation and erosion of molten silica based on our previous work[5~7] .

2 EXPERIMENTAL

2 .1 Raw materials

Si_2N_2O powder (pre-synthesized by the authors , containing cristobalite 7 % (mass fraction) or so , mean size 0 .88 μm , synthesizing method referred to Ref .[5]) ; N_2(high purity) ; Y_2O_3(A . R .) ; absolute alcohol (chemical purity) ; Si_3N_4 powder (α-$Si_3N_4 >$ 88 % , N > 38 %) .

2 .2 Procedure

Since there was 7 % or so cristobalite in 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 would be fabricated in further experiments . This was based on reaction (1) during sintering processes 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 in a plastic jar for 4 h , and then the mixture was dried . The dried mixture powder was sintered under 30 MPa pressure in 1 650 ℃ N_2 atmosphere . By altering sintering time , samples with different properties were therefore obtained .

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

$$\gamma = \rho_v / \rho_h \qquad (2)$$

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

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

where w_i is the mass percentage of i component in Si_2N_2O ceramics , and ρ is the theoretical density .

The mass gain of the ceramic sample would be

measured after it had been treated in the 1 000 ℃ air for hours. Then the resistance of the ceramic sample to oxidation would be assessed according to the mass gain in unit surface area.

The mass loss of the ceramic sample was measured after it had been impregnated for hours in molten silica, the components of which were similar to that of common glass. Then the resistance of the ceramic sample to erosion of molten silica was assessed according to the mass loss in unit surface area.

Micrograph of the fracture face was observed with a scanning electron microscope (SX-40).

3　RESULTS AND DISCUSSION

3.1　Results

The results and some experimental parameters are listed in Table 1. Fig.1 illustrates SEM micrograph of the fracture faces of sintered samples 1 ~ 3.

3.2　Resistance to oxidation

Table 1 shows that with respect to the same ceramic sample, the mass gain in unit surface (Δm_0) gradually increases with the oxidizing time; while with respect to the different ceramic samples, Δm_0 gradually decreases with the sintering time.

It is by affecting on the density and microstructure of the ceramic sample that the sintering time affects the resistance of the sample to oxidation. For ceramic materials, the resistance to oxidation mainly relates to the apparent porosity, and the relation formula between the oxidation mass gain and the surface area of the sample is as follows[8]:

$$\Delta m = KS = K(S_0 + S_p) \tag{4}$$

where Δm is the total mass gain of the sample; K is a constant; S is the total surface area; S_0 is the surface area determined by the geometric size; S_p is the surface area that related to the apparent porosity.

It is hypothesized that there are N apparent pores in unit surface of the sample and these pores are spherical with a mean radius r, then the total volume (V_{up}) of these pores is

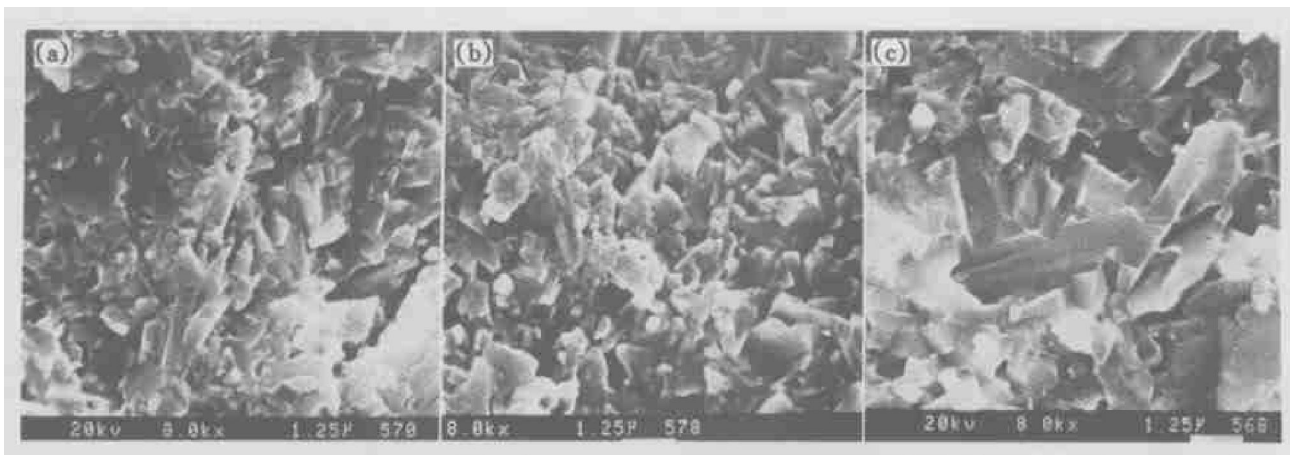$$V_{up} = N \cdot \pi r^3 \tag{5}$$

and their surface S_{up} is

$$S_{up} = N \cdot 4\pi r^2 \tag{6}$$

Moreover, it is further hypothesized that the apparent porosity is p, then

$$V_{up} = f \cdot p \tag{7}$$

where f is also a constant. The following formula is obtained from Formula (5), (6) and (7):

$$S_{up} = 3f \cdot p / r \tag{8}$$

Fig.1　SEM photographs of fracture faces of Si_2N_2O ceramic samples
(a) —Sample 1; (b) —Sample 2; (c) —Sample 3

Table 1　Chemical stability of Si_2N_2O ceramics

Samples	Sintering time/ h	Relative density/ %	Apparent porosity/ %	Oxidation resistance		Silica erosion resistance	
				time/ h	$\Delta m_0/(10 \text{ g} \cdot \text{m}^{-2})$	time/ h	$\Delta m_0/(10 \text{ g} \cdot \text{m}^{-2})$
6	0.5	94	1.8	20	0.52	10	- 0.34
				40	0.94	50	- 6.67
				100	1.20		
3	1.0	98	0.5	20	0.32	10	- 0.32
				40	0.76	50	- 5.36
				100	0.97		
7	1.5	100	0.2	20	0.24	10	- 0.29
				40	0.68	50	- 4.51
				100	0.70		

Then the following formula will be obtained :

$$S_p = S_0 \cdot S_{up} = S_0 \cdot 3 \, f \cdot p / r \qquad (9)$$

Combining (9) with (4) , then

$$\Delta m = K S_0 + S_0 \cdot 3 \, K f \cdot p / r \qquad (10)$$

In addition , the following Formula (11) will be further obtained :

$$\Delta m_0 = \Delta m / S_0 = K + 3 \, K f \cdot p / r \qquad (11)$$

It may be known from Formula (11) that the oxidation mass gain of unit surface of the sample (Δm_0) relates to the apparent porosity , and the more the apparent porosity is , the more the mass gain is . At the same time , the relevant data in Table 1 also illustrates that Δm_0 may reduces with decreasing apparent porosity during the oxidizing time of the same length .

Moreover , $Si_2 N_2 O$ may react with O_2 and further form a protective SiO_2 film in elevated temperature air , and the reaction process is controlled by the dispersing mechanism[9] . Because the partial pressure of O_2 is a constant in air , and the O_2 partial pressure needed in the reaction between O_2 and $Si_2 N_2 O$ is also a constant , the above dispersing process satisfies the edge conditions of an unsteady dispersing process with a constant source . For an unsteady dispersing process with a constant source , there is the following approximate relationship between the dispersed depth x and the dispersing time t[10] :

$$x = k \sqrt{Dt} \qquad (12)$$

where　k —constant ; D —dispersing coefficient .

Formula (12) indicates that x is approximately proportional to $\sqrt{t}$, that is , to elongate 1 time of x needs to elongate 4 times of dispersing time .

Moreover , it can be proved that the relationship between Δm_0 and x is linear . Δm_0 increases with the oxidizing time (i .e . the dispersing time) . However , the changing rate of Δm_0 gradually decreases . Comparing the relevant data in Table 1 , we can discover that the experimental results are in accordance with the above- mentioned analysis .

3 .3　Erosion to molten silica

The data in Table 1 also illustrates the relationship between the sintering time and the resistance to molten silica . For the same sample , the longer the eroding time is , the more the mass loss (Δm_s) is . While for different samples , it is also illustrated in data that Δm_s decreases with sintering time during eroding .

In fact , similar to the resistance to oxidation , the ceramic resistance to erosion of molten silica will also be affected by the density and microstructure of the sample . The higher the density is , and the lower the apparent porosity is , the stronger the resistance to

erosion of molten silica is , which has been proved by the data in Table 1 .

Moreover , maybe the glass phase in the grain boundary is easier to erode than $Si_2 N_2 O$ grains . Therefore , the bigger the grain is , the lower the quantity of the glass phases in the grain boundaries is . Carefully observing the three photographs in Fig . 1 , we may discover that the grains are bigger and bigger from Fig .1 (a) to (c) . In addition , combining the data in Table 1 , we can further discover that the erosion resistance of the sample is stronger and stronger from Sample 1 to Sample 3 . Therefore , that the results are in accordance with the above- mentioned analysis .

4　CONCLUSIONS

The resistance of $Si_2 N_2 O$ ceramics to oxidation/ erosion of molten silica related to its density , and may increase with increasing density or decreasing apparent porosity . Moreover , the resistance of erosion of molten silica relates to the amount of the grain boundaries in the sample surface . It can improve the resistance of erosion of molten silica to enhance the size of the grains and to reduce the amount of the grain boundaries in the sample surface .

REFERENCES

[1]　Boch P and Glandus J C . Elastic properties of silicon oxynitride [J] . J Mat Sci , 1979 , 14 : 397 ~ 383 .

[2]　Washburn Malcom E . Silicon oxynitride refractories [J] . J Am Ceram Soc , 1967 , 46(70) : 667 ~ 671 .

[3]　Bergman B and HUANG He- ping . The influence of different oxides on the formation of $Si_2 N_2 O$ from SiO_2 and $Si_3 N_4$[J] . J Europ Ceram Soc , 1990 , 6 : 3 ~ 8 .

[4]　O' Meara C , Sjöberg J , Doulop G , et al . Oxidation of pressless sintering $Si_2 N_2 O$ materials [J] . J Europ Ceram Soc , 1991 , 7 : 369 ~ 378 .

[5]　YAN Yu- hua , OUYANG Shi- xu and WANG Si- qing . Preparation of $Si_2 N_2 O$ powder from natural quartz powder [J] . The Chinese Journal of Nonferrous Metal , (in Chinese) , 1997 , 7(4) : 84 ~ 87 .

[6]　WANG Si- qing and YAN Yu- hua . Study on preparation and mechanical properties of $Si_2 N_2 O$ ceramics [J] . Trans Nonferrous Met Soc China , (To be accepted) .

[7]　WANG Si- qing and YAN Yu- hua . Effect of silicon source on synthesizing of $Si_2 N_2 O$ powder [J] . Jounal of Ceramics , (in Chinese) , 1997 , 18(3) : 154 ~ 157 .

[8]　Wada H and Wang L . Effect of gas phase on SiC and $Si_3 N_4$ formations from SiO_2[J] . J Mat Sci , 1992 , 27 : 1528 ~ 1563 .

[9]　LU Pei- wen . Silicon Physical [M] , (in Chinese) . Nanjing : Southeast University Press , 1991 . 311 .

[10]　YE Rui- lun and FANG Yong- han . Inorganic Material Physical Chemistry [M] , (in Chinese) . Beijing : China Construction Industry Press . 1984 . 244 .

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