[Article ID] 1003- 6326(2001)04- 0559- 04

Pressureless sintering of La-Y-Sialon ceramics and grain growth in later period of sintering ①

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[Abstract] The pressureless sintering process of Sialon ceramics added (1.5% La_2O_3 + 4.5% Y_2O_3) as sintering aids was studied. It is found that a β′-Sialon with relative density over 99% is obtained by sintering at 1 750 ℃ for 1 h. Crystal grain growth was observed at room temperature by SEM for the samples sintered at 1 800 ℃ holding for different time. It is proved that grain-growth along c-axis of β′-phase is a first priority, since (210) and (001) lattice plans have different activation energy. On the present conditions, logarithm of grain aspect ratio $\overline{L}/\overline{W}$ of average grain length $\overline{L}$ to average width $\overline{W}$ is in proportion to sintering time because of proportion of $\lg\overline{L}$ to sintering time and proportion of $\overline{W}$ to sintering time.

[Key words] Sialon; grain growth; pressureless sintering
[CLC number] TQ 174 **[Document code]** A

1 INTRODUCTION

Silicon nitride based ceramics are one kind of important advanced materials, a special attention has been paid by scientists. Since β-Si_3N_4 and β′-Sialon have large elongated grains, a self-strengthen and self-toughen effect maybe exist[1,2], therefore, many works on the grain growth of them have been dealt with[3~5]. It was discovered in 1979 by Lang[6] and Himsolt et al[7] that the content of β-phase in sintered Si_3N_4 ceramics increased as that of the α-phase in raw powder increasing and so the fraction toughness K_{IC} of the material was raised.

Tani[8] in 1986 and Mitomo[5] in 1990 reported that β′ phase Sialon ceramics had obvious self-strengthening effect. Since then, many works have been dealt with the relationship between fracture toughness and the microstructure of Si_3N_4[9]. Therefore, measuring the contents of β′ phase and the grain aspect ratios (L/W) are of significance for understanding the structures and properties of Sialon.

2 EXPERIMENTAL

Commodity Si_3N_4 powder with the specific surface area of 7.98 m^2/g had the content of α phase more than 87%, nitrogen 36.52% silicon 58.63%, free silicon 1.56%, oxygen 1.5%, and a little amount of impurities, such as C, Mg, Ca and K. Al_2O_3 powder was obtained by decomposing AR grade $Al(NO_3)_3\cdot 9H_2O$, and its mean particle size d_{50} by turbidimetry was 0.35 μm. AlN powder with the nitrogen content of 33%, mean particle size of 0.8 μm was purchased. The purities of Y_2O_3 and La_2O_3 powders were all higher than 99.999%. Taking Z= 2 in formula $Si_{6-Z}Al_ZO_ZN_{8-Z}$, dosimetric Si_3N_4, Al_2O_3, AlN and necessary amounts of Y_2O_3, La_2O_3 powders were mixed in mechanical mixer. Blanks were pressed in a steel die at 80 MPa and using polyvinyl alcohol (PVA) as pressing additive. Sintering was carried out in a graphite resistance furnace using mixed powders of Si_3N_4, Al_2O_3, AlN and BN as packing material.

The Z-values of sintered body were measured to be 1.73~ 1.94. The phase contents were measured by XRD semi-quantitative analysis. The grain sizes and aspect ratio were observed or determined by SEM. The result was an average value of over 300 grains measured in one sample.

3 RESULTS AND DISCUSSION

3.1 Effects of sintering temperature on phase composition and sintered density of Sialon

In Sialon ceramics, a new phase forms if the 5th element besides Si, Al, O and N exists in the system. In phase diagram, the new phase is a plane consist of Si_3N_4, 4/3 ($Al_2O_3\cdot$AlN) and MN·3AlN, the formula can be written as $M_x(Si, Al)_{12}(O, N)_{16}$ (M-Y, Mg, Ce, etc)[10,11]. Since it has the same crystal lattice as α-Si_3N_4, this phase is named α′ phase, but, the α′ isn't the low-temperature-form of β′ phase. Also the α′ and β′ can not transform each other. α′ reacts with Al_2O_3 or β′ reacts with AlN can produce β′ or α′ respectively[1]. Generally, the 5th element in Sialon system isn't avoidable, it may be the sintering aids (Y, La, Ce, Nd, Mg, etc), or the

① **[Received date]** 2000- 10- 23; **[Accepted date]** 2001- 01- 02

impurities (Ca, Mg, etc).

The experiment results are shown in Fig. 1. When the temperature is higher than 1600 ℃, the material is composed basically of β′ phase, but if the density of 99% is wanted, the sintering temperature must be higher than 1750 ℃.

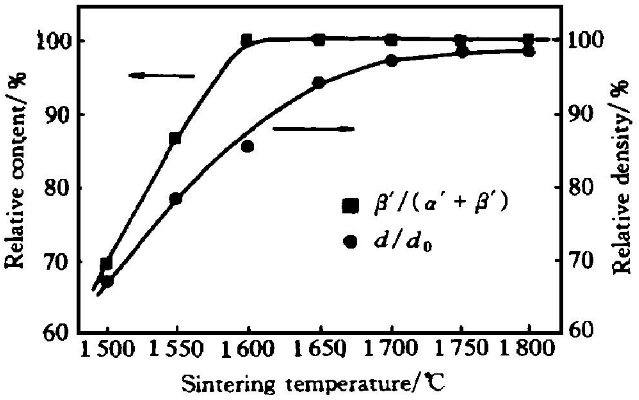


Fig. 1 Effects of sintering temperature on relative density and phase content of La-Y-Sialon

3.2 Relationship between grain size distribution and sintering time

The relationships between grain size distribution and sintering time are shown in Fig. 2~ Fig. 4. In these figures, E24, E34, E55 and E133 are the samples sintered at 1800 ℃ for 1, 2, 4 and 6h respectively. It can be found that the crystal grain length (L), grain width (W) and grain aspect ratio (L/W) increase with sintering time.

β′-Sialon has the same structure as β-Si_3N_4, which is built up of $[SiN_4]^{4-}$ hexagon along its c-axis one on the top of another, $ABAB$ construction, similar to berillite. β-Si_3N_4 lattice is shown as Fig. 5.

The atomic distance along [001] direction (c-axis), $d[001]$ = 0.290236 nm, along [210], $d[210]$ = 0.65775 nm. $d[210]$ is two times larger than $d[001]$. It can be seen that the atomic density of (001) plan is much lower than that of (210) plan, therefore, the grain boundary energy of (001) plan is much higher than that of (210) plan.

Lai et al[12] measured that the growth activation energy was 686 kJ/mol in [001] direction, and 882 kJ/mol in [210]. According to the principle, at the smallest energy surface the grain growth has a first priority, the surface of a single crystal exposed to growth environment should be the smallest energy surface. Comparing with (210) plan, (001) plan has more possible to be the grain boundary exposed in liquid phase. Then, the growth rate along [001] of β-

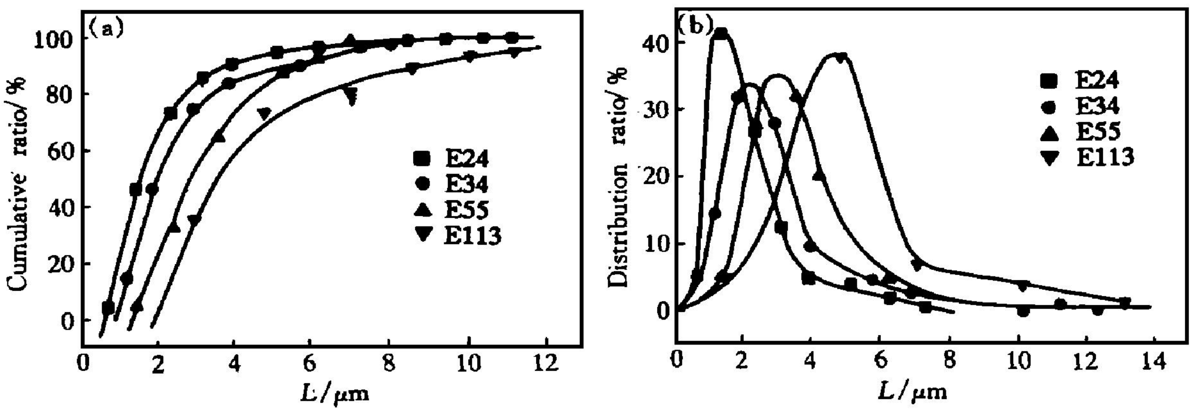


Fig. 2 Influence of sintering time on crystal grain length distribution of β′-phase
(a) —Cumulative curve; (b) —Distribution curve

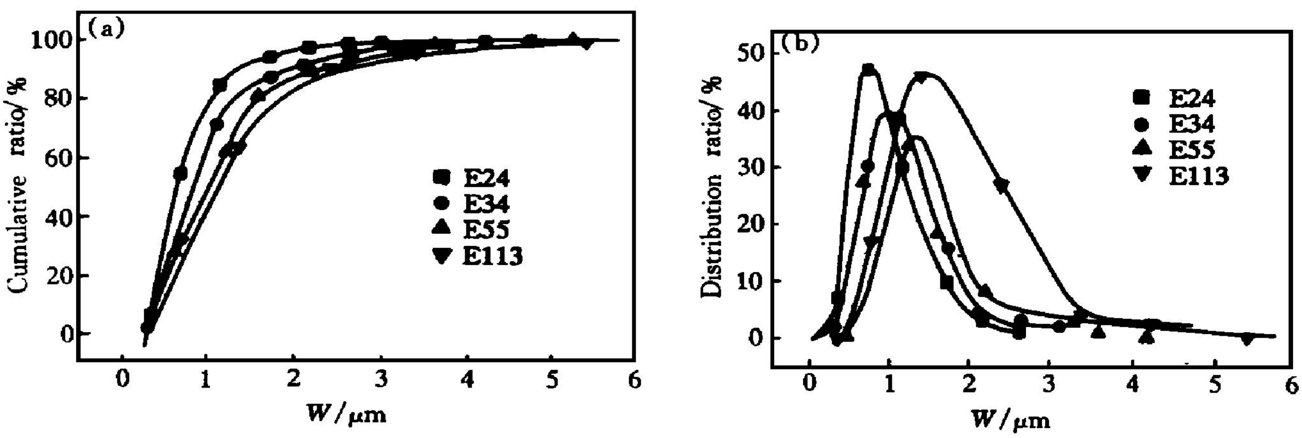
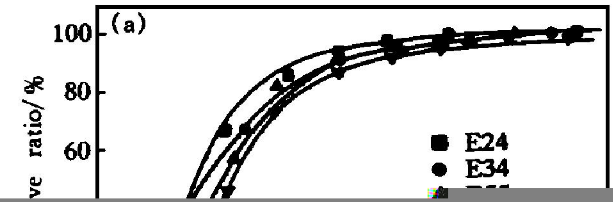


Fig. 3 Influence of sintering time on crystal grain width distribution of β′-phase
(a) —Cumulative curve; (b) —Distribution curve


(a)
100
80
60
ratio/ %
E24
E34


(b)
40
30
20
ratio/ %
E24
E34
E55
E113

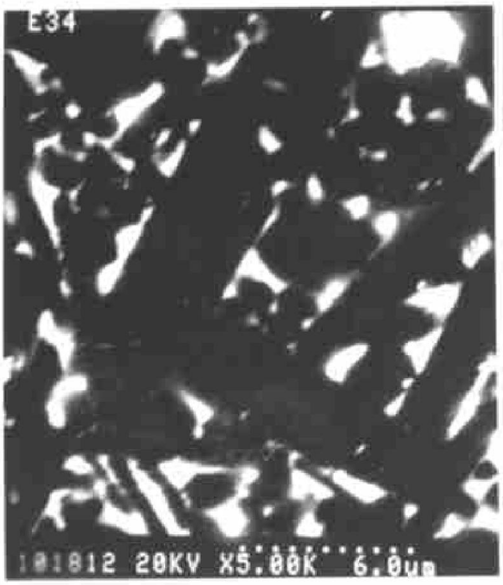


Fig. 8 Typical appearance of β′-La-Y-Sialon grain

4 CONCLUSIONS

1) A La-Y-Sialon ceramic with the density more than 99% was obtained by sintering at the temperature higher than 1 750 ℃ for 1 h and using (1.5% La_2O_3 + 4.5% Y_2O_3) as sintering aids.

2) When the sintering temperature is higher than 1 600 ℃ and the Z value equals 2, the La-Y-Sialon is composed of β′-phase only.

3) Grain growth along c-axis of β′-phase was a first priority. The logarithm of grain length and aspect ratio of β′-phase has a liner relationship with sintering time, but the width itself had a direct proportion to it.

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(Edited HE Xue-feng)