

Synthesis technology of spinel AlON

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Abstract: The high-purity AlON ceramics, AlON/ Al_2O_3 and AlON/AlN multiphase ceramics were prepared by pressureless sintering under nitrogen-based atmosphere with raw materials of Al_2O_3 , AlN and Al powders. The compositions of the phase were determined by XRD, the fracture appearance was analyzed by SEM. The results indicate: the aluminum oxynitride phase in the AlON ceramics and other multiphase ceramics exist in the form of $\text{Al}_5\text{O}_6\text{N}$, whose solid-solution zone is 33.4%(mole fraction) AlN belonging to spinel structures. The average grain size of high-purity AlON is about 3 μm . The grain boundary is smooth without other phases. The density is 2.82 g/cm^3 , the microhardness (10 N) and about bending strength are 1 470 MPa and 94 MPa, respectively.

Key words: pressureless sintering; spinel; aluminum oxynitride; high-purity

1 Introduction

The spinel aluminum oxynitride(AlON) is an important single-phase, stable solid solution ceramic of Al_2O_3 -AlN system, and has become a quite potential new material with unique performances. There are some excellent optical, physical, mechanical and chemical properties of AlON ceramics, in particular it can be sintered into the transparent one for its isotropy, and it is the optimum material for the infrared windows and covers to resist high temperature[1]. In addition, AlON ceramics are provided with high-temperature-resistance and chemical corrosion-resistance, with little wettability to liquified glass and hot metal, and with high resistance to heat shocks. Therefore, it is an excellent refractory[2-3]. Its transparency range covers infrared region (0.2 μm) to ultraviolet region (6.0 μm), and its strength and microhardness (2 N) reach 380 MPa and 110 MPa, respectively[1].

So far, AlN- Al_2O_3 binary system[4] has been discovered to possess kinds of nitrogen aluminum oxynitride phases. According to the crystal structures, these are divided into two groups approximately: one is the wurtzite structure, the other is the spinel structure. The solid solution zone of the later is 27%-40%(mole fraction) AlN. AlON ceramics are usually prepared by

carbothermal reduction method[5], solid phase reaction method[6] or self-propagating combustion method[7]. In carbothermal reduction method, AlON ceramics are difficult to densify, and CO will generate during the preparation. In solid phase reaction of AlN and Al_2O_3 powders, there are many problems, such as the high sintering temperature, the long reaction time and the multiphase AlON. The low-purity of AlON is the main disadvantage in self-propagating combustion method.

In this experiment, by choosing Al powders as sintering-aid, high-purity spinel AlON ceramics have been fabricated in pressureless sintering for nitrogen-based atmosphere with shorter reaction time and lower sintering temperature. It is discovered that AlON ceramics are composed of single-phase $\text{Al}_5\text{O}_6\text{N}$.

2 Experimental

2.1 Sample preparation

In this experiment, high purity Al_2O_3 , AlN, and Al powders were selected as the raw materials with grain size of 2, 0.5 and 1 μm , respectively. The raw materials were weighed and mixed according to Y1, Y2, Y3, Y4 (see Table 1). The mixtures were ground for 24 h with absolute alcohol as grind medium. After being discharged and dried, the mixtures were pressed by dry pressing method under 20 MPa. Finally the sintering

Table 1 Compositions of starting materials of various samples (mass fraction, %)

Sample No.	Al ₂ O ₃	AlN	Al
Y1	82	17	1
Y2	86	13	1
Y3	91	8	1
Y4	95	4	1

process was carried out in the multi-function sintering furnace. The vacuum sintering was performed under 1×10^{-3} Pa. The temperature was elevated with a heating rate of 6 °C /min. When the sintering temperature reached 1 000 °C, nitrogen gas was inflated to form atmospheric pressure. After the temperature reached 1 750 °C, the holding time was 1 h.

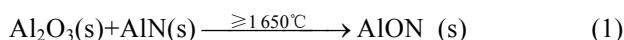
2.2 Properties testing

The density of samples was measured based on Archimedes drainage method. The phase structures were quantitatively analyzed by XRD (D/MAX-RB), which enabled to confirm the phase compositions during the reaction. The microstructure was observed and analyzed with scanning electron microscope (SEM Sirion200, Netherlands). The microhardness was determined with HV-1000 microhardness tester. The samples were machined into strips in dimension of 3 mm×4 mm×40 mm, and tested in three-point bend test with span of 30 mm and loading velocity of 0.5 mm/min.

3 Results and discussion

3.1 Phase analysis

Fig.1 shows the XRD patterns of different compositions after being sintered at 1 750 °C. No impurity peaks exist in Y3, in contrast the diffraction peaks of ALON are very strong, which indicates the high purity in the sintering body. Table 2 lists the quantitative analysis of the XRD patterns. It is clear from the patterns that if the content of ALON changes, the compositions of different sintered bodies will change. Y1 and Y2 are ALON/AlN multiphase ceramics, Y3 is high-purity ALON, and Y4 is ALON/Al₂O₃ multiphase ceramic. The ALON phase exists in the form of Al₅O₆N with 66.7%Al₂O₃ and 33.3% AlN (mole fraction). Besides, the solid solution zone of spinal structure is 27%–40% (mole fraction) AlN. Therefore, the sample belongs to the spinel aluminum oxynitride. The solution reaction is as follows:



According to calculation, 245 g of Al₅O₆N can be formed through the reaction of 204 g of Al₂O₃ and 41 g

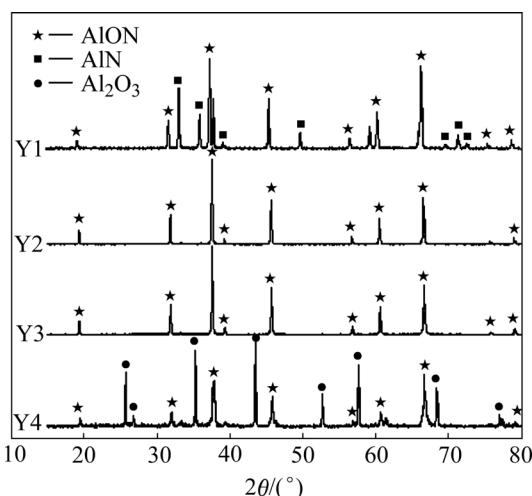
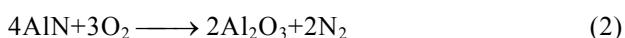


Fig.1 XRD patterns of ALON at 1 750 °C

Table 2 Quantitative analyses of ALON (mass fraction, %)

Sample No.	Al ₅ O ₆ N	AlN	Al ₂ O ₃
Y1	66.9	30.1	0
Y2	95.9	4.1	0
Y3	99.1	0.9	0
Y4	52.3	0	47.7

of AlN, which indicates the theoretical value of mass proportion between Al₂O₃ and AlN is 5:1. In contrast, the mass proportion of mixture Y3 that was prepared to ALON ceramics was 9:1, which suggested the dosage of AlN was shorter than the theoretical value. Thus, in the solid phase reaction of ALON, other reactions occurred at the same time. BACHELARD[8] has proposed that AlN produces Al₂O₃ at 300–700 °C, so the reaction is as follows:



Along with temperature increasing, under the condition of nitrogen and high temperature, reversible reaction will occur that part of Al₂O₃ produces AlN, then AlN will produce ALON with the Al₂O₃ again, which affects the mixture ratio between Al₂O₃ and AlN. Obviously, at 1 750 °C, if we prolong the reaction time of Y4, it is likely to obtain high-purity Al₅O₆N aluminum oxynitride ceramics.

3.2 Microtopograph analysis

Fig.2 shows the SEM micrographs of fractures of samples sintered, which shows great size differences between crystal grains.

Fig.2(a) shows that the average grain diameter is about 2 μm, and the size distribution is non-uniform with massive tiny particles, which is AlN particles judged from the particle size and the appearance. Also, there are many pores. In Fig.2(b) the average grain diameter is

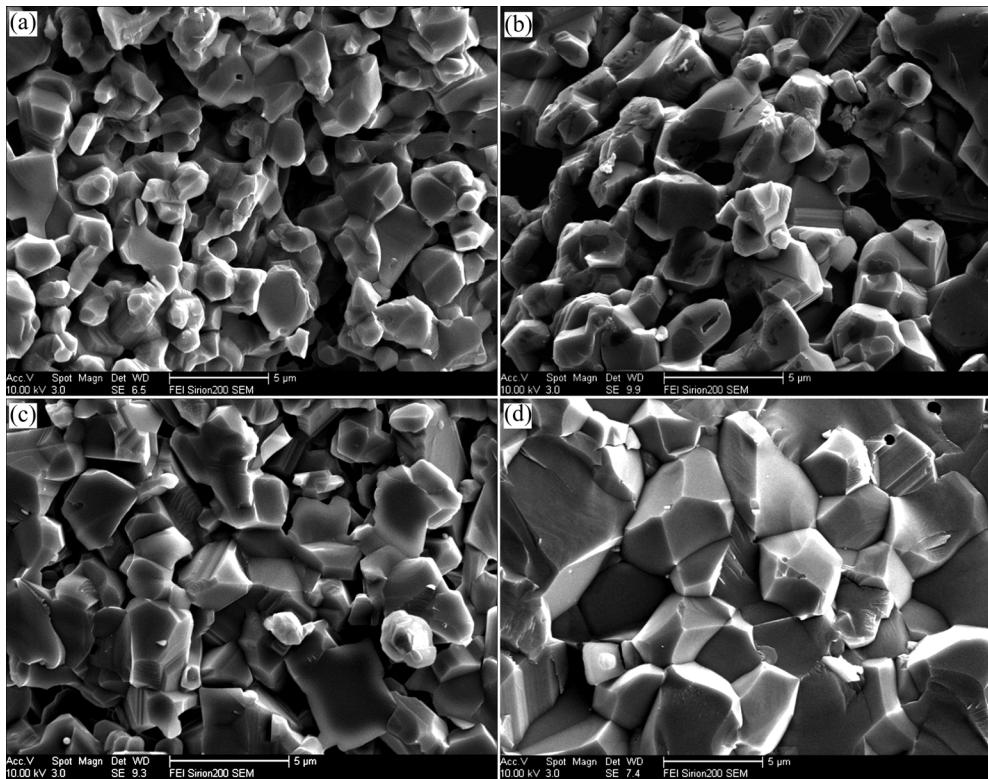


Fig.2 SEM photographs of AlON: (a) Sample Y1; (b) Sample Y2; (c) Sample Y3; (d) Sample Y4

about 3 μm , and the grain-size distribution is uniform. The characteristics of grains in Fig.2(c) are as follows: the grains distribute uniformly without abnormal growth, which indicates the crystals grow perfectly; there are no glass phase or crystallization phase between the grains; the average size of the particle size is approximately 3 μm , which is the smallest one in all the literatures that have been reported[9–10], and it is in favor of promoting the mechanical strength. The sample possesses compact structure, few pores, whose grains in Fig.2(d) are about 10 μm . This suggests that the increasing of Al_2O_3 leads to densification.

3.3 Properties of sintering body

The density, bending strength and microhardness of all samples after sintering reaction are listed in Table 3. It is evident that the samples(Y4) with low content of AlN are easy to sinter, and the sintering behavior is similar to Al_2O_3 . In contrast, when the content of AlN is higher (Y1, Y2, Y3), it is difficult to densify. The density of the high-purity AlON sample Y3 is 2.82 g/cm^3 , which is approximately 76% of the theoretical density of 3.71 g/cm^3 . Therefore, massive pores exist in the test sample. The density of the sample Y4 is 3.73 g/cm^3 , which is higher than the theoretical density of AlN of 3.26 g/cm^3 and the theoretical density of AlON, but smaller than the theoretical density of Al_2O_3 of 3.83 g/cm^3 . So that, in the sample there is Al_2O_3 , which is in agreement with the

Table 3 Properties of AlON

Sample	Density/ ($\text{g}\cdot\text{cm}^{-3}$)	Shrinkage/ %	Bending strength/ MPa	Microhardness (10 N)/ MPa
Y1	2.66	13	87	1 288
Y2	2.75	14	93	1 384
Y3	2.82	15	94	1 471
Y4	3.73	27	200	1 869

results of XRD. It is reported that the bending strength of AlON is higher than that of Al_2O_3 [11–12]. However, in the experiment, the bending strength of Y3 is less than that of Y4 because of higher porosity. Further analysis indicates that increasing density will be able to enhance the bending strength and microhardness.

4 Conclusions

- High-purity AlON ceramics was prepared by nitrogen and pressureless sintering at 1 750 °C for 1 h, which exists in the form of $\text{Al}_5\text{O}_6\text{N}$. The solid-melting zone is 33.4%(mole fraction) AlN, which indicates spinel structure. In the high-purity AlON, no obvious impurity phase can be determined. The grains bond directly, so there is no remarkable glass phase along the grain boundaries. The average diameter is 3 μm , the density, microhardness (10 N) and bending strength are 2.82 g/cm^3 , 1 470 MPa and 94 MPa, respectively.

2) The microhardness and bending strength of AlON/Al₂O₃ multiphase ceramics are higher than those of AlON/AlN multiphase ceramics and AlON ceramics.

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