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SYNTHESIS, PHASE TRANSFORMATION AND MECHANICAL PROPERTY OF SiAlON CERAMICS FROM COAL GANGUE

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Abstract

A simple and efficient method for preparation of SiAlON ceramics including β-SiAlON, O′-SiAlON and AlN polytypoid (15R and 12H) using reduction-nitridation of coal gangue and reducing agents at 1800K for 6h was described. The phase transformation of SiAlON at various atmospheres was discussed from thermodynamic and experimental analysis. Thermodynamic calculation revealed that different SiAlON phases could be synthesized at 1800K with the suitable atmosphere parameter Y ($Y = \lg(p_{O_2}/p^{\theta}) - \frac{2}{3}\lg(p_{N_2}/p^{\theta})$ *).*

Low Y value was beneficial to synthesis of β-SiAlON. The experimental result showed that β-SiAlON ceramics with the content of 90% was fabricated at strong reductive atmosphere in flowing nitrogen. O′-SiAlON with the content of 85% can be synthesized in flowing nitrogen atmosphere. In view of AlN polytypoid, the suitable condition to produce 15R was flowing nitrogen and 12H was formed at a weak reductive atmosphere. The mechanical properties of SiAlON ceramics synthesized under optimum conditions, i.e., modules of rupture (MOR) at room temperature, have been reported.

Key words: *SiAlON, synthesis, phase transformation, mechanical properties, coal gangue.*

1. Introduction

SiAlONs are compounds of silicon, aluminum, oxygen and nitrogen which have been widely used as engineering ceramics, cutting tools and refractory materials because of their excellent properties, e.g. high fracture toughness, strength and corrosion resistance[1-6]. They occur in a range of compositions with structures closely related to those of the oxide or nitride parent material from which they are derived by substitution of Al for Si and O for N. The majority of SiAlON phases are β-SiAlON, O′-SiAlON, X-phase and AlN polytypoid. β-SiAlON is structurally related to β-Si_3N_4 and has the composition of $Si_{6-z}Al_zO_zN_{8-z}$ where z ranges from 0 to 4.2. O′-SiAlON is a Si-rich phase which has a structure derived from Si_2N_2O with the composition of $Si_{2-x}Al_xO_xN_{2-x}$ where x ranges from 0 to 0.4. The structure of X-phase SiAlON, $Si_{12}Al_{18}O_{39}N_8$, is similar to mullite and exists over a narrow solid solution range between Si_3N_4 and mullite.

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The composition of AlN polytypoid is between β-SiAlON and AlN. There are many polytypoid phases with wurtzite-type structures having compositions of M_mX_{m+1}(M=Al, Si; X=N, O).

SiAlON ceramics can be prepared by using pure oxides and nitrides as starting materials which are at high cost [7-10]. In recent years, some work has been done on preparing SiAlON from natural aluminosilicate minerals, such as kaolinite, clay, diatomite, andalusite, zeolite, fly ash, and coal gangue, etc. which may be of cost effectiveness [11-17]. However, due to the complicate compositions of natural aluminosilicate minerals, the experimental condition to synthesis SiAlON is difficult to control [1, 17-20]. How to optimize the experiment parameters for SiAlON synthesis will be of great importance and has been aroused the interest of the researchers. Most of the related work is focused on synthesis of β-SiAlON and O′- SiAlON materials due to their wide solid substitution range and super properties. Zhang [16] reported to synthesize O′- SiAlON by reduction-nitridation from coal gangue and optimized the preparation parameters by computer pattern recognition program. Xu et. al. [21] optimized the experimental parameters for β-SiAlON powder and β-SiAlON bonded corundum from natural clay using optimal analysis by orthogonal method. Yamakawa et al. [22] proposed a technique of gas reduction-nitridation (GRN) to produce high-purity β-SiAlON powder using zeolite as raw material. Yue at. al. [17] synthesized high-purity β-SiAlON powder using coal gangue based on thermodynamic calculation. Works about optimizing the experimental conditions to synthesize SiAlON phases, especially AlN polytypoid from natural minerals is seldom reported in the literature.

Since SiAlON ceramics is practically employed as engineering material, its mechanical properties play an important role and should be investigated. Most work is focused on investigating the mechanical property of monolithic SiAlON ceramics prepared from pure oxides and nitrides [23-25]. Studies concerning the mechanical properties of SiAlON ceramics prepared from natural materials are scarce.

With the developing of mining industry, more and more mining wastes have been produced, for instance coal gangue. Since the main chemical compositions of coal gangue are silica and alumina, it can be used as raw material to synthesize SiAlON. In the present work, SiAlON ceramics including β-SiAlON, O′- SiAlON and AlN polytypoid (15R and 12H) were synthesized at 1800K for 6h in a controllable way using Chinese coal gangue and reducing agents as raw material. The suitable synthesis conditions were discussed from thermodynamic analysis and experiments. The mechanical properties of SiAlON ceramics, MOR at room temperature were investigated. This work is currently considered as the baseline of SiAlON ceramics synthesized from natural aluminosilicate minerals.

2. Experimental

Chinese coal gangue was used as starting material and its chemical compositions were as follows (mass %): SiO_2 (64.84%), Al_2O_3 (27.70%), Fe_2O_3 (3.04%), CaO (0.72%), and MgO (1.11%). Other materials such as activated charcoal (A.R., Sinopharm chemical reagent Co. Ltd, China), silicon powder (74μm; 99.0% purity A.R., Sinopharm chemical reagent Co.Ltd, China) and aluminum powder (74μm; 99.5% purity ; A.R., Beijing chemical Co., China) were used as reduction-nitridation agents. SiAlON phases can be synthesized by the following equations:

$$4SiO_2 + Al_2O_3 + 4Al + 5C + 3.67N_2 \rightarrow 1.67Si_{2.4}Al_{3.6}O_{3.6}N_{4.4}(\beta\text{-}SiAlON) + 5CO \quad (1)$$

$$4SiO_2 + Al_2O_3 + 4Si + 4C + 4N_2 \rightarrow 5Si_{1.6}Al_{0.4}O_{1.4}N_{1.6}(O'\text{-}SiAlON) + 4CO \quad (2)$$

$$4SiO_2 + Al_2O_3 + 14Al + 3C + 8N_2 \rightarrow 4SiAl_4O_2N_4(15R) + 3CO \quad (3)$$

$$4SiO_2 + Al_2O_3 + 18Al + 3C + 10N_2 \rightarrow 4SiAl_5O_2N_5(12H) + 3CO \quad (4)$$

The above mixtures were ball milled according to formulations (Table 1) with ethanol as medium. The slurry was dried and pressed into pellets of 47mm×6mm×6mm in size at the pressure of 100MPa. Twelve specimens (B#, O#, R# and H#) were for tests in different atmosphere. The specimens were placed into an alumina crucible and then sintered at 1800K for 6h. The crystalline phases were identified by X-ray diffraction analysis (XRD: Rigaku DMAX-RB diffractometer) with Cukα radiation. The morphology of cross section of samples was examined by the field-emission scanning electron microscopy (FE-SEM, ZEISS) equipped with energy-dispersive spectroscopy (EDS). The bulk density of the fabricated ceramics was determined using Archimedes' principle. The mechanical property of sample, i.e., MOR at room temperature was investigated using 3-point bending method. The equation is described as follows:

$$\sigma_f = \frac{3Fl}{2bh^2} \quad (5)$$

Where σ_f is the bending strength of material at room temperature (MPa), F is the load force at fracture (N), l is the length of support span (m), b is the specimen width (m) and h is the specimen thickness (m).

Table 1. Formulations of specimens

Specimen code	Formulation/ mass%			
	Coal gangue	Al	C	Si
B#(β-SiAlON)	68.8	20.0	11.2	-
O#(O'-SiAlON)	69.8	-	9.1	21.1
R#(15R)	47.2	48.2	4.6	-
H#(12H)	41.5	54.5	4.0	-

3. Results and discussion

3.1. Thermodynamic calculation

According to the phase diagram of Si_3N_4-AlN-SiO_2-Al_2O_3 (Fig.1) [1, 17], X-phase and O′-SiAlON exist between the phases of oxides and β-SiAlON, indicating that X-phase and O′-SiAlON may appear during β-SiAlON synthesis depending on the reaction atmosphere. The transformation equations can be described as follows:

$$\beta - SiAlON(0 < z \le 1.2) + \frac{3}{2}O_2 \leftrightarrow 3O' - SiAlON + N_2 \quad (6)$$

$$6\beta - SiAlON(1.2 < z \le 3.6) + (7.2 + 1.5z)O_2 \leftrightarrow (27 - 7.5z)O' - SiAlON + (0.5z - 0.6)X - phase + (4.8 + z)N_2 \quad (7)$$

The standard Gibbs free energies of β-SiAlON and O′-SiAlON at 1800K can be assessed by using the thermodynamic quasi-parabolic rules [26] as follows:

$$\Delta_f G^{\Theta}_{\beta-SiAlON}(0\langle z \le 4.2) = 7576.7z^2 - 417333.3z - 231140\,(J/mol) \quad (9)$$

$$\Delta_f G^{\Theta}_{O'-SiAlON}(0\langle x \le 0.4) = 99838.5x^2 - 354623.5x - 428625\,(J/mol) \quad (10)$$

Setting the ratio of Al to Si in molar, *6n(Al)/n(Si+Al)* as X axis and *lg(P_{O2}/P^{θ})-2/3lg(P_{N2}/P^{θ})* as Y axis, the stable phases as a function of oxygen partial pressure at 1800K can be calculated from Eq.(6)-(8) and the results are shown in Fig.2. From Fig.2, it can be seen that β-SiAlON exists only at extra low oxygen partial pressure. By comparison, O′-SiAlON can exist stably at a little higher oxygen partial pressure.

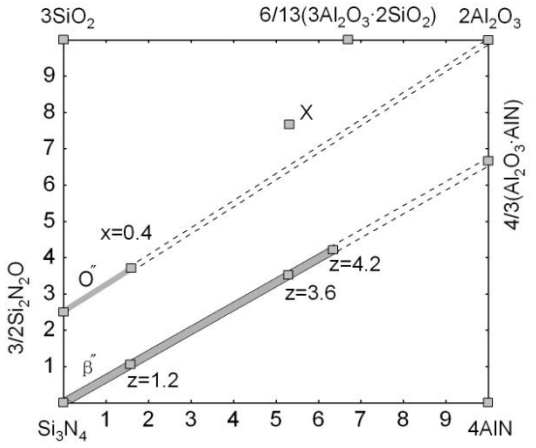

Figure 1. Phase diagram of Si_3N_4-AlN-SiO_2-Al_2O_3 system [1, 17]

To obtain low oxygen partial pressure, extra carbon can be added because it will react with oxygen by following reaction:

$$C + 0.5O_2(g) = CO(g) \quad (11)$$

When the equation reaches equilibrium, *$\Delta G_{(P,\ T)} = 0$*. The following equation can be obtained:

$$\lg(\frac{p_{O_2}}{p^{\theta}}) = 2\lg(\frac{p_{CO}}{p^{\theta}}) - 8.965 - (\frac{11972}{T}) \quad (12)$$

According to Eq. (12), the oxygen partial pressure is much smaller than that of CO at high temperature, indicating that the extra low oxygen partial pressure can be obtained by adding carbon.

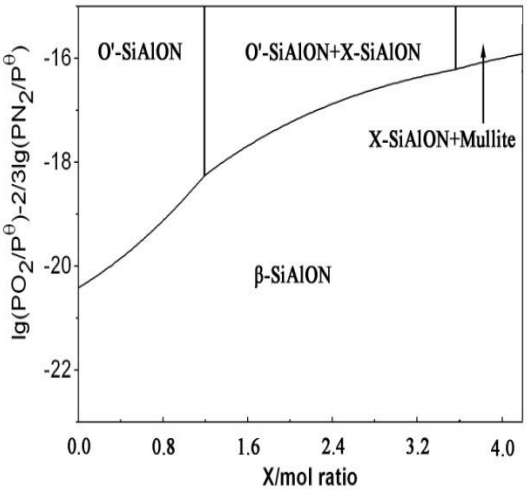

Figure 2. The stable phase region of SiAlON at 1800K

3.2. Synthesis of SiAlON ceramics

According to the thermodynamic analysis, atmosphere plays an important role on the compositions of SiAlON phase [27, 28]. In the experiments, three different conditions, i.e., (a) Weak reductive atmosphere obtained using graphite crucible in flowing air atmosphere (AC); (b) Neutral atmosphere obtained using alumina crucible in flowing high purity nitrogen atmosphere (≥99.999%) (NA); (c) Strong reductive atmosphere obtained using graphite crucible in flowing high purity nitrogen atmosphere (≥99.999%) (NC) were adopted to investigate the effect of atmosphere on phase composition of SiAlON.

In view of Specimen B#, the phases obtained under the above three conditions were analyzed by XRD.

Fig. 3a was the phase composition of sample synthesized under weak reductive atmosphere (AC), from which it can be seen that no characteristic peaks of β-SiAlON appeared and the phases of mullite, silicon carbide (SiC) and corundum (Al_2O_3) existed instead under this condition. For the sample synthesized under neutral atmosphere (NA), the main phases were X-phase and corundum (Al_2O_3) (Fig.3b). Under the strong reductive atmosphere (NC), the main phases of β-SiAlON and Al_2O_3 with trace amount were produced as shown in Fig.3c. Therefore, β-SiAlON ceramics can be produced under NC atmosphere, which was in agreement with the thermodynamic analysis. The z value of β-SiAlON was calculated to be 2.64 according to the empirical equation [29], which was lower than the designed values, 3.6. As reported in the literature [30], increasing the sintering temperature or prolonging the reaction time may obtain β-SiAlON with higher z value.

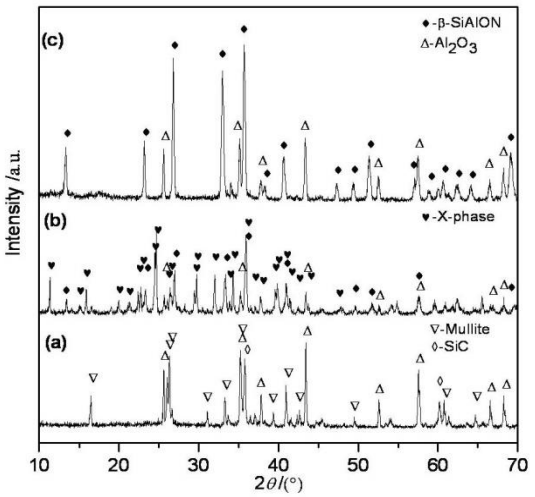

Figure 3. XRD patterns of specimen B# reacted at different atmosphere (a) AC; (b) NA; (c) NC

Fig.4 showed XRD results of specimen O# synthesized under the three conditions using Si as internal standard. By comparison, the phase of O'-SiAlON as the main product appeared under neutral atmosphere (NA) (Fig.4b).

The relative content of the constituents of reaction product could be estimated approximately by the following formula:

$$P_i\% = A_i / \sum A_{ij} \quad (13)$$

where P_i% is the relative content of i composition, A_i is the absolute integral area of the strongest characteristic peak of i composition, and $\sum A_{ij}$ is the summation of the integral area of characteristic peaks for all crystal phases in the reaction product. The relative content of O'-SiAlON synthesized under NA condition was calculated to be about 85% (shown in Table 2), indicating the suitable condition to produce O'-SiAlON with higher content was neutral atmosphere (NA).

O'-SiAlON formation process may be considered to proceed in two stages: the formation of Si_2N_2O and O'-SiAlON synthesis. Si_2N_2O can be formed by the two following ways [16]:

(1)

$$Si(s) = Si(l)(1685K) \quad (14)$$

$$3Si(l) + SiO_2(s) + 2N_2(g) \rightarrow 2Si_2N_2O \quad (15)$$

(2)

$$3Si(l) + 2N_2(g) \rightarrow Si_3N_4(s) \quad (16)$$

$$Si_3N_4(s) + SiO_2(s) = 2Si_2N_2O \quad (17)$$

O'-SiAlON can be produced by the reaction between Si_2N_2O and Al_2O_3 as follows:

$$0.8Si_2N_2O + 0.2Al_2O_3 \rightarrow Si_{1.6}Al_{0.4}O_{1.4}N_{1.6}(O' - SiAlON) \quad (18)$$

According to the above equations, Si_2N_2O or Si_3N_4 was the intermediate product to form O'-SiAlON. While they may reacted with mullite to produce X-phase, which has been confirmed by XRD analysis (Fig.4b).

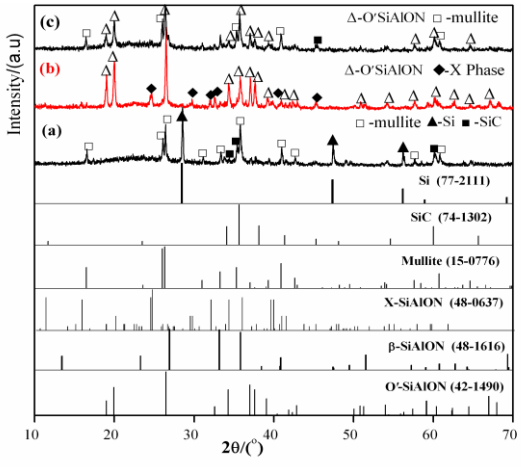

Figure 4. XRD patterns of specimen O# reacted at different atmosphere (a) AC; (b) NA; (c) NC

In view of specimen R#, the phase of 15R appeared under both AC and NA conditions (Fig.5a and b) while its relative content was higher (>75%) under neutral atmosphere (NA) (Table 2). Besides 15R phase, the phases of β-SiAlON and Al_2O_3 also existed. For specimen H#, the phase of 12H only appeared at weak reductive atmosphere (AC) (Fig.6a) and its relative content was calculated to be about 75%. Impurities also existed during SiAlON synthesis. The main reason was probably that the chemical impurities such as Fe_2O_3, CaO and MgO existed in coal gangue. They easily became liquid phase at high reaction temperature, i.e. 1800K, and caused intermediate products to grow and finally existed in the product. This has been verified by XRD analysis. Although impurities existed during SiAlON synthesis, this was the first work reported in the literature to produce SiAlON especially the phases of 15R and 12H using natural aluminosilicate minerals as raw material.

Table 2. Phase analysis of specimens synthesized at 1800K at different atmosphere *

Specimen code	Atmosphere	Phase composition
O′-SiAlON	AC	Si(vs),M(s), S(s), O′ (m)
	NA	**O′ (vs), X(vm)**
	NC	O′ (vs), S(s), M(m), β′ (w)
15R	AC	A(vs), 15R(s), S(w)
	NA	**15R(vs), β′ (s), A(s)**
	NC	A(vs), β′ (s), X(m)
12H	**AC**	**12H(vs), 15R(s), A(s)**
	NA	A(vs), 15R(vs), β′ (w)
	NC	A(vs), β′ (m); X(vw)

*β′: β-SiAlON; O′: O′-SiAlON; X: X-phase; M: mullite; S: SiC; A: Al_2O_3; 15R:15R-AlN polytypoid; 12H: 12H-AlN polytypoid; Vs: very strong; s: strong; m: medium; w: weak; vw: very weak

In view of specimen R#, the phase of 15R appeared under both AC and NA conditions (Fig.5a and b) while its relative content was higher (>75%) under neutral atmosphere (NA) (Table 2). Besides 15R phase, the phases of β-SiAlON and Al_2O_3 also existed. For specimen H#, the phase of 12H only appeared at weak reductive atmosphere (AC) (Fig.6a) and its relative content was calculated to be about 75%.

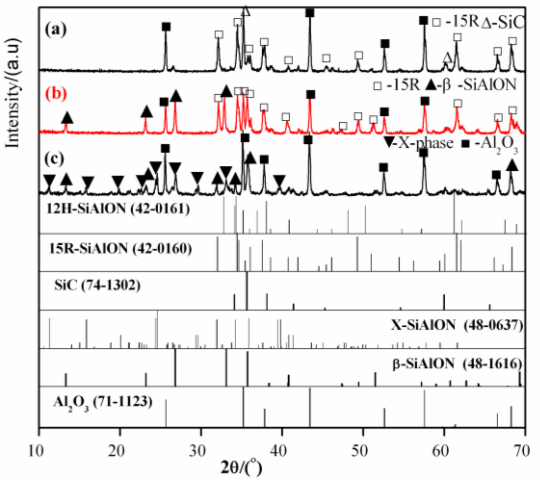

Figure 5. XRD patterns of specimen R# reacted at different atmosphere (a) AC; (b) NA; (c) NC

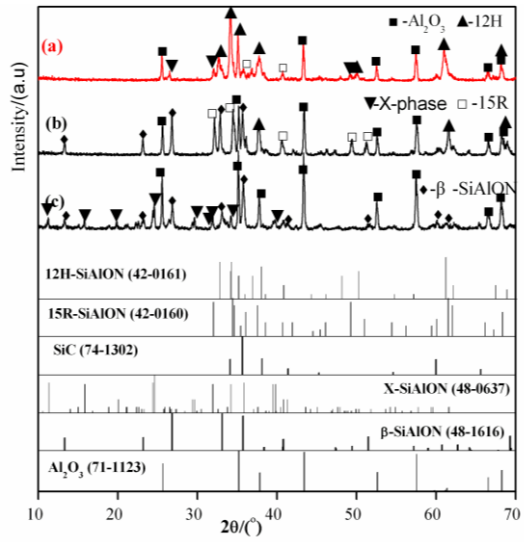

Figure 6. XRD patterns of specimen H# reacted at different atmosphere (a) AC; (b) NA; (c) NC

3.3. Microstructure characterization of SiAlON ceramics

Typical microstructure of the fracture surface of β-SiAlON ceramics was shown in Fig.7a, which existed in hexagonal crystal system with rod-shape at the top.

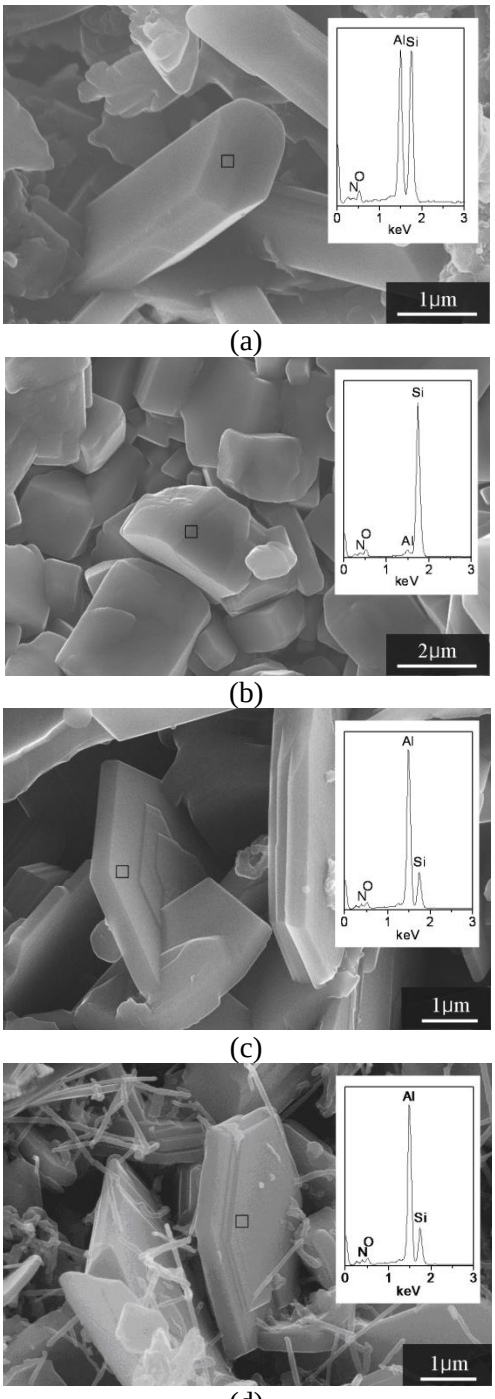

Figure 7. Typical SEM images of (a) β-SiAlON with EDS; (b) O′-SiAlON with EDS; (c) 15R with EDS; (d) 12H with EDS

EDS analysis showed the composition of Si, Al, O and N. O′-SiAlON consisted of a microstructure comprising of equiaxed grain with the size in the range of 1-5μm (Fig.7b). Fig.7c showed the microstructure of 15R, from which it can be seen that 15R had perfect crystals with structure of regular hexagonal flakes and the thickness of the laminar grains was about 0.2-0.3μm. As for the phase of 12H, the microstructure was similar to 15R as shown in Fig.7d.

3.4. Mechanical property of SiAlON ceramics

The bulk densities of the synthesized SiAlON ceramics under the suitable conditions were measured to be 1.69 (β-SiAlON), 2.09(O'-SiAlON), 1.98 (15R) and 2.01g/cm^3 (12H) respectively (as shown in Table 3). MOR at room temperature of SiAlON ceramics was determined using 3-point bending method and the results were shown in Table 3.

Table 3. Physical properties of SiAlON ceramics

Sample	Physical properties	
	Bulk density (g/cm^3)	MOR (MPa)
β-SiAlON	1.69	17.1
O′-SiAlON	2.09	34.6
15R	1.98	38.1
12H	2.01	35.9

Among this, MOR of β-SiAlON ceramics was lowest. The main reason was probably that large amount of carbon as a reductive agent (up to 11% as shown in Table 1) was employed during the synthesis process of β-SiAlON ceramics. The reaction of carbon involved tended to produce gas product and thus caused β-SiAlON ceramics synthesized to possess lower density and MOR. In addition, the mechanical property of SiAlON ceramics is not as good as that reported in the literature [21-24]. This was probably caused by the processing method [23, 24]. Advanced processing technique such as hot isostatic pressing (HIP) can be applied to obtain higher MOR.

4. Conclusions

SiAlON ceramics including β-SiAlON, O′-SiAlON, 15R and 12H were synthesized using Chinese coal gangue as raw materials by direct reduction-nitridation method at 1800K for 6h. The effect of different atmospheres on the formation of SiAlON has been investigated both from thermodynamic analysis and experimental results.

The synthesis parameters of SiAlON ceramics based on thermodynamic calculation revealed that β-SiAlON was stable at extra low oxygen partial pressure. While O′-SiAlON could exist at a little higher oxygen partial pressure. The experimental results showed that β-SiAlON ceramics with high content (about 85%) can be synthesized in strong reductive atmosphere. O′-SiAlON and 15R with the content of about 85% and 75% respectively can be produced in neutral atmosphere. While the weak reductive atmosphere was beneficial to produce 12H phase and the content synthesized under this condition was about 75%. All the ceramics synthesized in the experiment possessed the typical microstructure of SiAlON phases reported in the literature.

The mechanical property of SiAlON ceramics was investigated. MOR at room temperature of SiAlON ceramics were 17.1 (β-SiAlON), 34.6(O'-SiAlON), 38.1(15R) and 35.9Mpa (12H) respectively.

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