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Synthesis and characterization of single-crystalline phase Li-α-Sialon

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Abstract

Single-crystallize phase Li-α-Sialon with equiaxial morphology has been successfully synthesized by solid state reaction at 1700 °C for 1 h under a N_2 atmosphere. The effects of additions SiO_2 and Al_2O_3, holding time at 1050 °C and packing powders, on the phase compositions and Li contents of products have been investigated by XRD, SEM, EDS and ICP-OES. The results showed that additions SiO_2 and Al_2O_3, holding time at 1050 °C and packing powders played an important role in retarding the vaporization of lithium and forming Li-α-Sialon, where the former two ways were by formation of more Li-containing liquid while the latter was by providing a source of Li-containing vapor and increasing partial pressure of Li in the surrounding gaseous environment resulting in preventing volatilization of Li from the sample. However, there were more or less AlN, $AlSi_{0.5}O_{2.5}$, β-Sialon present in the products when these factors were ignored.

Keywords: A. Powders: solid state reaction; B. X-ray methods; D. Sialon; Retarding vaporization of lithium

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1. Introduction

Since their discovery in the 1970s, Sialon ceramics have attracted intensive attention because of their excellent mechanical properties even at high temperatures, good corrosion resistance and outstanding thermal shock resistance [1–3]. α-Sialon, as one well known type of Sialon, was represented by the formula of $M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, where $(m + n)$ Si–N bonds are replaced by m Al–N and n Al–O bonds, and the valence discrepancy introduced in α-Sialon is counter-balanced by a v-valent metal cation M^{v+}, such as Li^+, Ca^{2+}, Mg^{2+}, Y^{3+} and some rare-earth ions, and with $x = m/v$ [4,5]. Compared with β-Sialon ($Si_{6-z}Al_zO_zN_{8-z}$), α-Sialon promises high hardness because its structure consists of a longer stacking sequence of ABCD than the AB in β-Sialon, giving longer Burgers vector for dislocations, which makes it particularly suitable for cutting tool or bearing parts [6–8]. Furthermore, the amount of intergranular phase can be reduced by the transient liquid phase being absorbed into the matrix of a-Sialon phase during sintering, which makes it an excellent structural ceramic for high temperature applications [9]. To date, most of work has concentrated on the Ca^{2+}, Y^{3+} and Ln-α-Sialon systems [10–12].

Since Li-α-Sialon was reported among the first a′ phases [4], it has received limited attention, due to mainly the difficulty in preparing pure Li-α-Sialon and the problem of volatilization of lithium associated with the densification [13]. However, the eutectic temperature of Li_2O–SiO_2–Al_2O_3 in the Li–Si–Al–O–N system (1050 °C) is lower than those of the related calcium, yttrium and rare-earth systems (1170 °C × ∼1350 °C) [13], which implies that the formation and densification temperature of α-Sialon in the former system may be lower than those in the latter ones [14,15]. Accordingly, the study on Li-α-Sialon has been attracted increasing attention in recent years. Shen et al. [16,17] studied the rapid densification and deformation of Li-α-Sialon ceramics by spark plasma sintering (SPS) which significantly reduced Li evaporation. The products obtained mainly consisted of Li-α-Sialon, but contained some minor phases such as β-Sialon and AlN. Yu et al. [15,18] prepared single phase Li-α-Sialon by hot-press sintering and studied the single phase formation region of Li-α-Sialon. Meanwhile, they also prepared Li-α-Sialon at 1700 °C for 1 h by solid state reaction. However, the product is usually associated with a small amount of impurities by this method due to the serious volatilization of lithium.

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For the purpose of synthesizing single-crystalline phase Li-α-Sialon by solid state reaction, in this present work, the measures of adding important additions of SiO_2 and Al_2O_3, holding for 1 h at 1050 °C and packing powders have been taken to retard the volatilization of lithium, and their effects have been discussed. Because the phase composition formed is strongly dependent on the lithium content and because lithium is easily lost by volatilization, we have determined the Li content in the prepared compacts by the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) method.

2. Experimental procedures

2.1. Starting materials

The starting raw material powders were Si_3N_4 (99.7 wt.%; α-phase >93.8 wt.%, Shanghai Anseml Fine Ceramic Co., Ltd., China), AlN (98 wt.% pure, Advanced Technology & Materials Co., Ltd., China), Al_2O_3 (A.R., Beijing F&F Chemical Industrial Co., Ltd., China), SiO_2 (A.R., Beijing F&F Chemical Industrial Co., Ltd., China) and Li_2CO_3 (99.99 wt.% pure, General Research Institute Nonferrous Metals, China). In the preparation of the samples, the oxygen content of the Si_3N_4 (2.9 wt.% SiO_2) and AlN (1.6 wt.% Al_2O_3) powders was taken into account when formulating the mixtures. Li-α-Sialon samples with different *m*, *n* values in the general formula $M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ were investigated in the present work as indicated in Table 1. It should be explained that the sample without additional SiO_2 and Al_2O_3 were also investigated as a control test.

2.2. Sample preparation

The starting powders, in a batch of 30 g, were mixed with 60 g of ethanol in a ball mill for 12 h. The homogenous slurry was initially naturally dried for 6 h, and then dried in an oven at 70 °C for 24 h. The mixtures obtained were forced through a 300 mesh sieve. 2.0 g of the sieved powder mixture was die-pressed into of 10 mm under 22 MPa. The specimens were contained in a graphite crucible and fired in a graphite furnace under a N_2 atmosphere (99.99 wt.% purity) at 1700 °C for 1 h. Pure BN powder and a mixture of 50 wt.% BN and 50 wt.% corresponding raw material powders (abbreviated BN–Li–Al–Si–O–N) were chosen as the packing powders during this heat treatment, meanwhile, the specimens without packing powders were also studied. In order to retard the volatilization of lithium, during the heating process, we took the measure of holding time at 1050 °C, which is the eutectic temperature of the Li_2O–SiO_2–Al_2O_3 system [16]. Hence, the heating process was performed in two stages, i.e., heating-up from ambient temperature to 1050 °C at the rate of 10 °C/min under 0.12 MPa of N_2 pressure and an isothermal holding time of 1 h, then raised to 1700 °C at the rate of 5 °C/min under 0.60 MPa of N_2 and an isothermal holding time of 1 h. After being calcined the samples were furnace-cooled. For comparison, the case without holding time at 1050 °C was also investigated.

2.3. Sample characterization

Phase compositions of as-synthesized products were identified by X-ray diffraction (XRD; CuKα_1, D8-Advance, Bruker, Germany). Based on the XRD results, the lattice parameters of α-Sialon were calculated. Fractured surfaces of the samples were thermally etched at 1400 °C for 0.5 h and subsequently examined by scanning electron microscopy (SEM; JSM-6460LV, JEOL, Japan) equipped with an energy dispersive spectroscopy detector (EDS; INCA, Oxford Instrument).

Lithium content was determined by Inductively Coupled Plasma Optical Emission Spectrometry (IRIS Intrepid II XSP, Thermo fisher, America). Standard Li solutions were used to construct the calibration curve. 0.050 g pulverized sample was mixed with 15 ml 40 wt.% HF + 3 ml 65 wt.% HNO_3 and digested in Teflon breakers at 200 °C for 3 h. Then the sample solutions added 6 ml 36 wt.% HCl + 2 ml 65 wt.% HNO_3 + 2 ml 72 wt.% $HClO_4$ were digested at 220 °C. When the white smoking of $HClO_4$ exhausted, 10 ml HNO_3 was added to dissolve the salts. The obtained solutions were diluted to 25 ml. The error in the measurement of lithium content, using this process, is estimated to be ±0.03 wt.%, based on repeated analyses of identical samples.

3. Results and discussion

The phase assemblages of different (*m*, *n*) samples with and without additional SiO_2 and Al_2O_3 in BN–Li–Si–Al–O–N packing powders prepared at 1700 °C for 1 h during 1050 °C holding for 1 h are tabulated in Table 1. It shows that without additional SiO_2 and Al_2O_3, the reaction products mainly

Table 1
Starting compositions and phase assemblages.

Sample (*m*, *n*)	Batch composition (wt.%)				Addition (wt.%)		Phase assemblage[a]
	Li_2CO_3	Si_3N_4	AlN	Al_2O_3	SiO_2	Al_2O_3	
(1.0,1.0)	6.29	79.35	13.94	0.42	2.30	0.22	α (s), AlN (vw)/α
(1.3,1.2)	8.03	74.01	17.11	0.85	2.15	0.27	α (s), 15R (vw)/α
(1.5,1.5)	9.10	68.84	20.15	1.91	1.99	0.32	α (s), 15R (w)/α
(1.5,0.75)	9.21	75.49	15.30	-	2.19	0.24	α (s), Eu (vw)/α

α, Li-α-Sialon; Eu, Eucryptite ($LiAlSiO_4$); 15R ($SiAl_4O_2N_4$); s, strong; w, weak; vw, very weak.

[a] Phase assemblage of samples were prepared at 1700 °C for 1 h in BN–Li–Si–Al–O–N packing powders and holding time at 1050 °C for 1 h without (before a slash) and with (after a slash) additional SiO_2 and Al_2O_3.

consisted of Li-α-Sialon, associated with some minor phases such as unreacted AlN in the (1.0, 1.0) sample, 15R ($SiAl_4O_2N_4$) in the (1.3, 1.2) and (1.5, 1.5) sample, and eucryptite ($LiAlSiO_4$) in the (1.5, 0.75) sample, while single-crystalline phase Li-α-Sialon in the samples with additional SiO_2 and Al_2O_3. The typical XRD patterns of reaction sequences in the (1.0, 1.0) sample with and without additional SiO_2 and Al_2O_3 are shown in Fig. 1a and b. Meanwhile, Fig. 1 also indicates the XRD patterns of the (1.0, 1.0) sample prepared with (Fig. 1a) and without (Fig. 1c) holding time for 1 h at 1050 °C. There was single-crystalline phase Li-α-Sialon in the sample with holding time, but a little of $AlSi_{0.5}O_{2.5}$ in the sample without holding time. The phase compositions of the (1.0, 1.0) samples in different packing powders are shown in Fig. 1a, d and e. When mixtures of BN–Li–Al–Si–O–N powders were employed as the packing powders, single-crystalline phase Li-α-Sialon could be prepared at 1700 °C for 1 h with additional SiO_2 and Al_2O_3, while a little of β-Sialon occurred in the production with some minor unreacted AlN when BN packing powder was used instead of BN–Li–Al–Si–O–N packing powders, and the peak of β-Sialon is enhanced in the sample without packing powders.

In order to verify the role played by the additional SiO_2 and Al_2O_3, holding time at 1050 °C and packing powders in retarding the volatilization of Li, the lithium content of as-synthesis samples was determined by ICP-OES, shown in Fig. 2. It indicates that the lithium content in product of (1.0, 1.0) sample under different conditions is respectively lower than the theoretical content of 1.236 wt.%. The result illustrated that there was some extent of volatilization of lithium to synthesis Li-α-Sialon by solid state reaction. Nevertheless, the lithium content of the (1.0, 1.0) sample with additional SiO_2 and Al_2O_3, BN–Li–Si–Al–O–N packing powders and holding time at 1050 °C (0.833 wt.%, Fig. 2a) is respectively higher than that of without additional SiO_2 and Al_2O_3 (0.601 wt.%, Fig. 2b), with BN packing powder (0.397 wt.%, Fig. 2c), without packing powder (0.259 wt.%, Fig. 2d), as well as without holding time (0.529 wt.%, Fig. 2e).

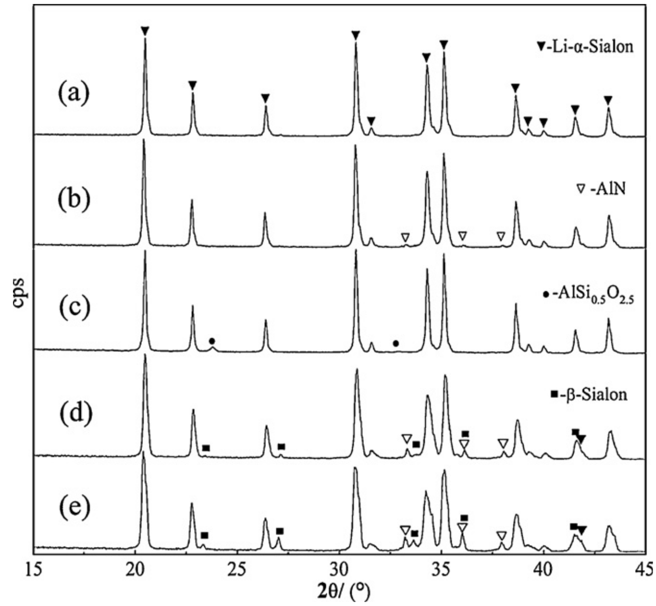

Fig. 1. XRD patterns of the (1.0, 1.0) sample prepared at 1700 °C for 1 h under different conditions (a) A + C + F, (b) B + C + F, (c) A + C + G, (d) A + D + F, (e) A + E + F. A/B, with or without additional SiO_2 and Al_2O_3; C, in BN–Li–Si–Al–O–N; D, in BN; E, without packing powders; F/G, with or without holding time at 1050 °C.

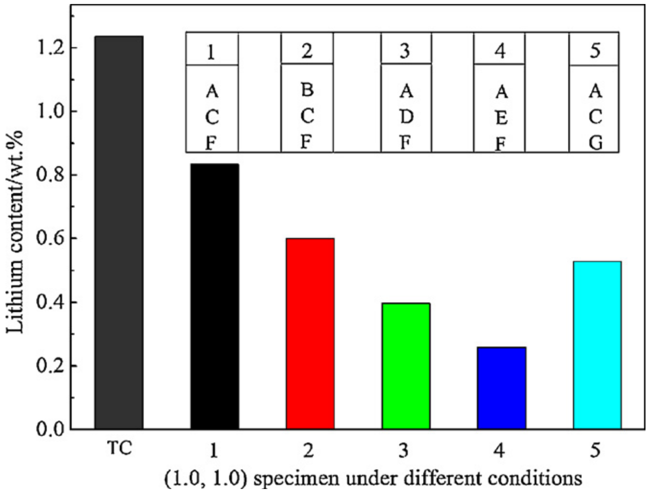

Fig. 2. Lithium content in of (1.0, 1.0) specimen under different conditions determined by ICP-OES. TC, theoretical content; A/B, with or without additional SiO_2 and Al_2O_3; C, in BN–Li–Si–Al–O–N; D, in BN; E, without packing powders; F/G, with or without holding time at 1050 °C.

In addition to the phase compositions and lithium content, the lattice parameters of as-synthesized Li-α-Sialon were also affected by the additional SiO_2 and Al_2O_3. It can be seen from Fig. 3 that the lattice parameters of Li-α-Sialon in the samples with additional SiO_2 and Al_2O_3 were respectively higher than those of the samples without additional SiO_2 and Al_2O_3 at corresponding (*m*, *n*) values. The reason for these increased lattice parameters should be attributed to the increasing lithium content of the sample with additional SiO_2 and Al_2O_3, which agrees with the report by Kuang et al. [14], revealing that lattice parameters of Li-α-Sialon ($Li_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$) increase with increasing *x*.

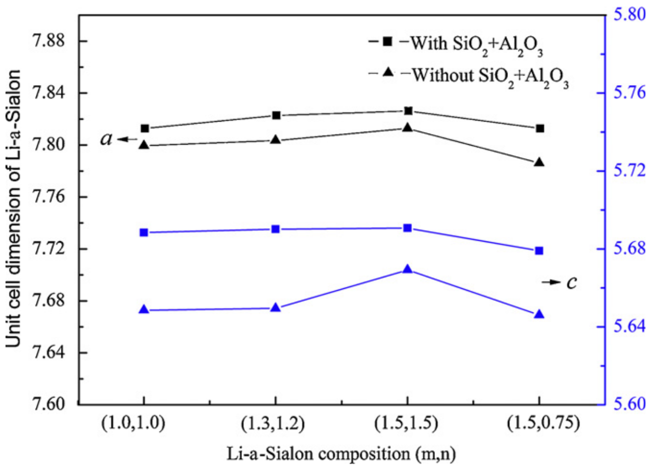

Fig. 3. Lattice parameters of Li-α-Sialon synthesized under different conditions.

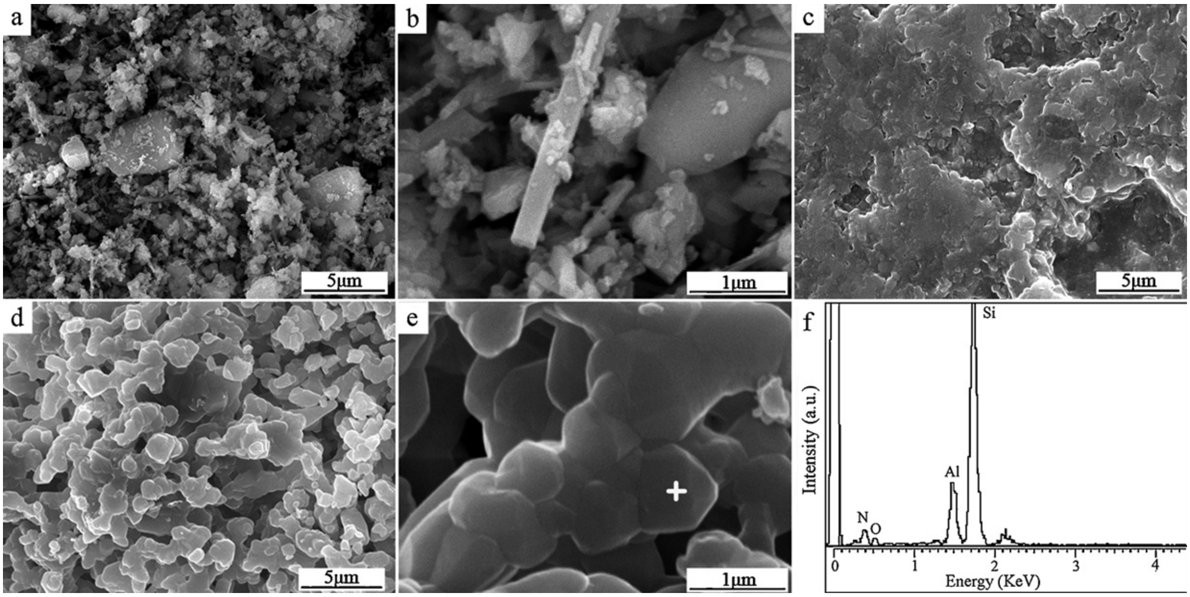

Fig. 4. Micrographs of (1.0, 1.0) sample before and after solid state reaction at 1700 °C with additional SiO_2 and Al_2O_3 and holding time at 1050 °C for 1 h in BN–Si–Al–O–N packing powders. (a and b) Raw materials, (c) fractured surface after being sintered, (d and e) thermally etched fracture surface, and (f) EDS for a Li-α-Sialon crystal in (e).

Moreover, we also observed the microstructures of these different (m, n) samples before and after solid state reaction at 1700 °C with additional SiO_2 and Al_2O_3 in BN–Si–Al–O–N packing powders which were similar, and the typical SEM micrographs of (1.0, 1.0) sample are shown in Fig. 4. SEM observations reveal that there were lots of micro-size grains (≤ 1 μm), associated with large AlN grains with sizes of 3–4 μm, long Si_3N_4 grains with sizes of 2–5 μm in the start mixed powders (Fig. 4a and b). Obviously, the sample containing only the Li-α-Sialon crystalline phase also contained appreciable amounts of liquid/glass, seen from the fractured surfaces in Fig. 4c. In order to reveal the Li-α-Sialon grain morphology, the sample was thermally etched at 1400 °C for 0.5 h in nitrogen atmosphere, and the morphologies of the etched fracture surface are shown in Fig. 4d and e. The Li-α-Sialon grains exhibited equiaxial morphology with sub-micron size of 0.5–1 μm. Because of its low atomic number, the peak of Li was not detected in the EDS pattern of Li-α-Sialon grain (Fig. 4f).

The above results shows that the three measures, i.e., adding important additions of SiO_2 and Al_2O_3, holding for 1 h at 1050 °C and packing powders, played an important role in retarding the volatilization of lithium. An understanding of how they retarded is necessary. Previous investigations have shown that the reaction process of Li-α-Sialon using a powder mixture of Si_3N_4, AlN and Li_2CO_3, was initially the Li_2O produced from the decomposition of Li_2CO_3 reacted with SiO_2 and Al_2O_3 (on the surfaces of the nitride powders) to produce a Li-containing liquid at low temperature. Then some Si_3N_4 dissolved in the liquid and β-LiSiON(Al) phase formed. As the temperature increased, AlN and increasing Si_3N_4 dissolved in the liquid phase which gradually became more nitrogen rich and diffused towards the limiting composition in equilibrium with α-Sialon, and reprecipitated into Li-α-Sialon [15]. The main reactions are expected to be:

$$Li_2O + SiO_2 + Al_2O_3 \rightarrow Li - Al - Si - O_{(liquid)} \tag{1}$$

$$Li - Al - Si - O_{(liquid)} + Si_3N_4 \rightarrow \beta\text{-LiSiON(Al)} + \text{liquid} \tag{2}$$

$$\beta\text{-LiSiON(Al)} + Si_3N_4 + AlN \overset{\text{Liquid1}}{\longrightarrow} Li - \alpha\text{-sialon} + \text{liquid2} \tag{3}$$

From above reaction process of Li-α-Sialon, it was noticed that measures leading to formation of more Li-containing liquid could effectively retard the volatilization of lithium. Combined the result of XRD and ICP-OES analysis, it is believed that the measures of adding additional SiO_2 and Al_2O_3 and holding time at 1050 °C, the eutectic temperature of Li_2O–SiO_2–Al_2O_3, could facilitate the generation of the Li-containing liquid, thereby, retard the volatilization of lithium. As for the third measure, the additions of 50% Li–Al–Si–O–N powders (corresponding raw powders) in the BN–Li–Al–Si–O–N packing powders provided a source of Li-containing vapor, and the increased partial pressure of Li in the surrounding gaseous environment prevented volatilization of Li from the sample.

Furthermore, it is well known that the formation mechanism of α-Sialon is proposed to proceed in liquid-phase via dissolution–diffusion–reprecipitation. After the completion of the transformation from α-Si_3N_4 to α-Sialon, the growth of α-Sialon grains follows an Ostwald ripening process through a transient liquid [16–18]. In this work, it is inferred that the reprecipitation process proceeded by nucleation of Li-α-Sialon onto the starting particles via dissolution and consumption of the bigger AlN and longer Si_3N_4 relative to the size of as-synthesized Li-α-Sialon (Fig. 4). When additional SiO_2 and

Al_2O_3 were added into the reaction system, additional Li-rich liquid formed can enhance dissolution of Si_3N_4 and AlN grains, reduce the liquid viscosity and accelerate the diffusion rate, thus, assist the formation of Li-α-Sialon. Consequently, the Li-α-Sialon formed should be richer in Li, Al, O, and therefore have larger lattice parameters.

4. Conclusions

Single-crystalline phase Li-α-Sialon has been successfully synthesized by solid state reaction at 1700 °C for 1 h and holding time at 1050 °C for 1 h in BN–Li–Si–Al–O–N packing powders, with additional SiO_2 and Al_2O_3 in raw powders. The Li-α-Sialon grains exhibited equiaxial morphology with submicron size of 0.5–1 μm. Additional SiO_2 and Al_2O_3, holding time at 1050 °C and BN–Li–Al–Si–O–N packing powders played an important role of retarding the vaporization of lithium and forming single-crystalline phase Li-α-Sialon with bigger lattice parameters, where the first and second ways were by formation of more Li-containing liquid whereas the third was by providing a source of Li-containing vapor and increasing partial pressure of Li in the surrounding gaseous environment resulting in preventing volatilization of Li from the sample.

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