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Synthesis of Mg-α-sialon from the mixture of silicon, aluminum and magnesia powders in a flowing nitrogen atmosphere

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Abstract Synthesis of Mg-α-Sialon has been investigated by the mixture of silicon, aluminum and magnesia powders in a flowing nitrogen atmosphere in the range of 1300–1600 °C, when Mg-α-Sialon is designed with a chemical formulation of $Mg_xSi_{12-3x}Al_{3x}O_xN_{16-x}$ in present work. The results showed that Mg-α-sialon initially occurred at 1400 °C and basically increased with elevated temperatures. For the samples of $x = 0.6$, 0.8 and 1.0 the products mainly consisted of Mg-α-Sialon with small amounts of Si, AlN and 21R AlN-polytypoid phases at 1600° C. However, in final products of $x = 1.2$, 1.4 and 1.6 only a little of Mg-α-Sialon formed and a great amount of Si remained in these samples at all the fired temperatures. Fortunately, the content of Mg-α-Sialon in these samples were obviously increased by adding a small amount of α-Si_3N_4 as seeds before nitridation.

Introduction

Sialon ceramics have attracted intensive attentions of materials scientists for their excellent mechanical properties even at high temperatures, good corrosion resistance and outstanding thermal shock resistance since they were discovered in the 1970s [1]. α-sialon were observed shortly after β-sialon with the general formula $M_xSi_{12\text{-m–n}}Al_{m+\text{-}n}O_nN_{16\text{–n}}$ where M is one of the cations such as Li^+, Mg^{2+}, Ca^{2+}, Y^{3+} or most rare-earth metals (excluding La, Ce, Pr and Eu). α-sialon is solid solution based on α-Si_3N_4, and has a unit cell comprising four molecules of Si_3N_4. In α-sialon, m (Si–N) bonds are replaced by the much longer (Al–N) bonds and n (Si–N) bonds are replaced by the similar sized (Al–O) bonds. One of the most important advantages of α-sialon is that the amount of intergranular phase is reduced by the transient liquid phase being absorbed into the matrix of α-sialon phase during sintering, which makes it to be developed as an excellent structure ceramic in high temperature applications [2, 3].

α-sialon ceramics are usually achieved by direct solid-state reaction, carbothermal reduction and nitridation or self-propagating high-temperature synthesis (SHS) [4–7]. However, the costs of α-sialon ceramics are usually much higher than those of most oxide based ceramics owing to their manufacturing processes, which lead to the practical use of α-sialon ceramics in small scales even until today. Therefore, the search for an alternative route to synthesize α-sialon materials is still being pursued intensively. Direct nitriding of the powder mixture of Si, Al and some additives to synthesize α-sialon in a flowing nitrogen atmosphere may be a promising approach owing to its following characteristics: (1) cheaper raw materials, Si_3N_4 and AlN can be in-situ derived from Si and Al; (2) lower synthesis temperature, exothermic reactions of Si and Al with N_2 gas are likely to decrease the synthesis temperature; (3) lower facility demand, only a common nitridation furnace is adequate.

Mg-α-sialon ceramics and its composite materials are promising materials in high temperature applications such as special refractories and engineering ceramics in association with the prominent characteristics that Mg^{2+}, is easily available in nature, compared with Li^+, Y^{3+}, rare earth ions. However, Mg-α-sialon is seldom synthesized except that Zhang et al. [8] derived Mg-α-sialon powder from talc and

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halloysite clay minerals by carbothermal reduction nitridation. Also, (Ca, Mg)-α-sialon was synthesized by hot pressing at high temperatures [9–12]. Here it is reported that Mg-α-sialon has been directly synthesized from the mixture of silicon, aluminum and fused magnesia powder in a flowing nitrogen atmosphere lower than 1600 °C.

Experimental

The compositions studied in our experiment are located in so-called Mg-α-sialon plane and fulfil m = 2n, so Mg-α-sialon is formulated to $Mg_xSi_{12-3x}Al_{3x}O_xN_{16-x}$. The value of $x = 0.4$, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6 were selected for sample compositions. Starting powder mixtures were prepared by using Si powder (98.5% Si, < 88 μm), Al powder (99.0% Al, < 88 μm) and fused magnesia powder (98.2% MgO, < 88 μm). Powder mixtures were prepared by using planetary ball mill. The well-mixed powder were compacted into $\phi 20 \times 20$ mm cylindrical samples at a pressure of 100 Mpa. The green compacts were set into a nitridation furnace, and first dwelled at 700 °C and 1300 °C for 3 h, then up to 1400, 1500, 1600 °C for 3 h, respectively, at heating rate of 2.5 °C/min in a flowing N_2 gas ($N_2 \geq 99.9\%$, $O_2 \leq 0.005\%$) with a flowrate of 1 L/min. The phase compositions of all the products were analyzed by X-ray diffraction (XRD, Philip, X′ Pert Pro). The semi-quantitative estimation of Mg-α-sialon phase was based on Eq. (1) according to the integrated intensities of the diffraction lines of (201) for Mg-α-sialon, (111) for Si, (100) for AlN, (110) for 21R and (200) for β-Si_3N_4. Similar equations were used to estimate the contents of Si, AlN, and 21R phases in samples. The morphology of samples was characterized by scanning electron microscopy (SEM, QUANTA 400) linked with an energy dispersive spectrometer (EDS, INCA).

$$\text{Mg}-\alpha-\text{sialon}\% = \frac{I_{\text{Mg}-\alpha-\text{sialon}}(201)}{I_{\text{Mg}-\alpha-\text{sialon}}(201) + I_{\text{Si}}(111) + I_{\text{AlN}}(100) + I_{21\text{R}}(110) + I_{\beta-\text{Si3N4}}(200)} \times 100\% \tag{1}$$

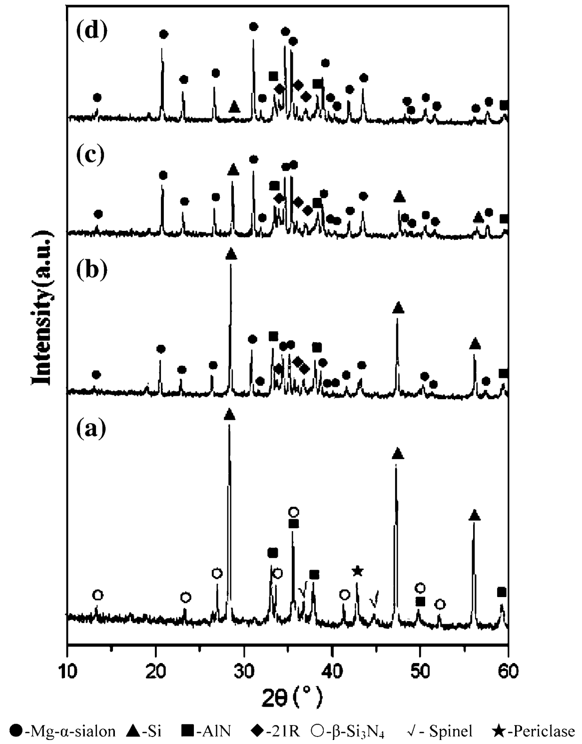


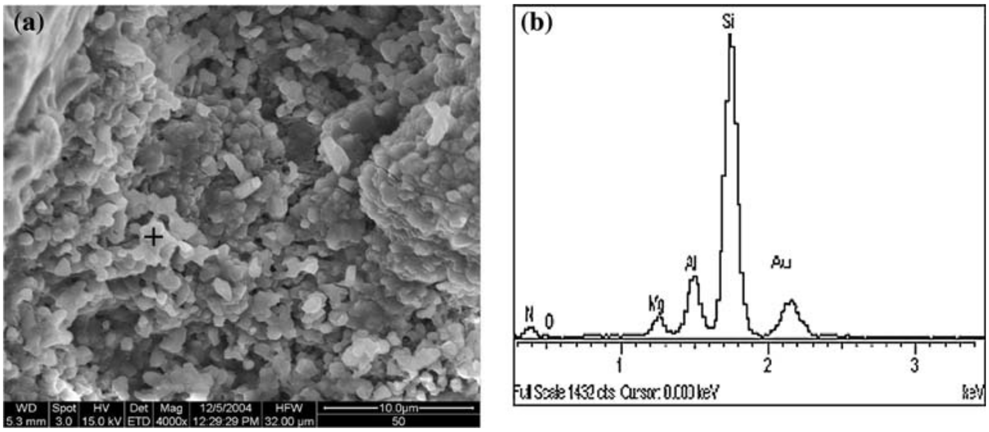
Fig. 1 XRD patterns of $x = 1.0$ sample fired at 1300 °C (**a**), 1400 °C (**b**), 1500 °C (**c**) and 1600 °C(**d**)

Results and discussions

All the samples fired in the range of 1300–1600 °C were determined by X ray diffraction. XRD patterns of $x = 1.0$ sample fired at different temperatures are shown in Fig. 1. At 1300 °C, Si, β-Si_3N_4, AlN and periclase are found as main crystalline phases with a small amount of spinel in the product. At 1400 °C, Mg-α-sialon initially occurs together with 21R phase. At the same time, β-Si_3N_4 and periclase are no longer found. At 1500 °C, much Mg-α-sialon phase occurs with the decrease of Si and AlN phases. At 1600 °C, Mg-α-sialon becomes main phase in final product. So the main reactions perhaps involved in the samples of $x = 1.0$ are presumed as follows: At lower than temperature of 1300 °C, Al, Si react with N_2 into AlN and Si_3N_4, accompanying with a small amount of spinel phase due to the reaction between MgO and Al_2O_3 derived from Al oxidized by MgO around Al particles in the mixtures or by a little O_2 in flowing N_2. At high than 1400 °C, much Si converts into Si_3N_4 and reacts with AlN and MgO to form Mg-α-sialon phase. Meanwhile, the occurrence of 21R is likely to be associated with the enriched AlN and liquid phase in some part of samples at high temperature [13].

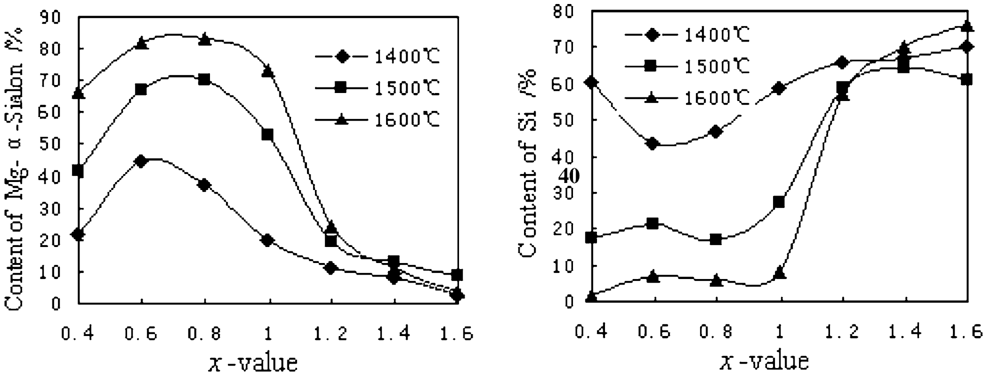
The ruptured morphology of $x = 1.0$ sample fired at 1600 °C is shown in Fig. 2. Mg-α-sialon particles have

Fig. 2 Morphology and typical EDS spectra of Mg-α-sialon in x = 1.0 sample fired at 1600 °C

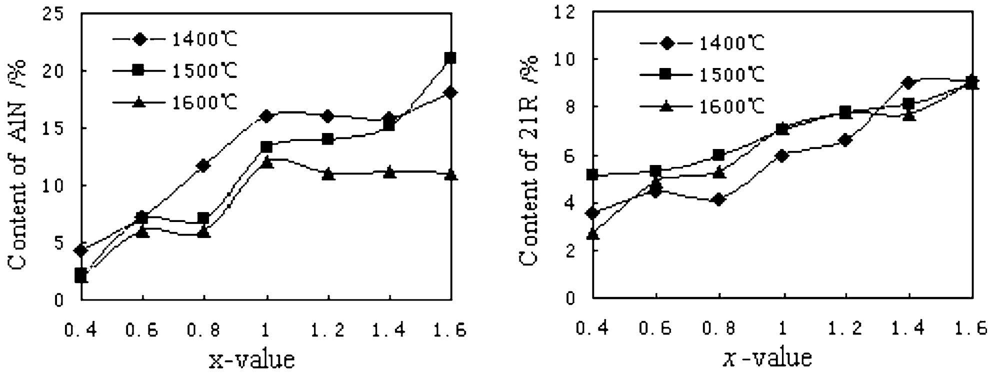


grown up into 2–5 μm, which could also be confirmed that particles contain Si, Al, Mg, O, N and Au elements by EDS analysis (Fig. 2b). Au element out of them results from Au thin film at the surface of the sample, which is coated so as to observe clearly the morphology by SEM.

Generally, α-sialon is produced in transient liquid phase in liquid sintering process. Zhou et al. [14] found that a transient phase initially occurred and then Ca-α-sialon formed in liquid phase. Also, a transient phase formed during hot pressing of α-Si_3N_4 and MgO [15]. In our experiment it was found that a great amount of Si phase existed in samples at nitridation temperatures, which were higher than its melting point (~1400 °C), at the same time Mg-α-sialon phase began to appear in all samples. So, the formation of Mg-α-sialon was likely related to Si liquid phase or other transient liquid phase of Mg-Si-Al-O-N system, which was confirmed by other researchers [15, 16]. It is



(a) Mg-α-sialon **(b)** Si



(c) AlN **(d)** 21R

Fig. 3 The relative contents of phases in all samples fired at 1400, 1500 and 1600 °C proposed that as received AlN, Si_3N_4 and MgO solve in these liquid phases, then Mg-α-sialon precipitates out of the saturated liquid phase.

Mg-α-sialon phase is also found in other samples and increases with elevated temperature except for $x = 1.4$ and 1.6. The semi-quantitative contents of Mg-α-sialon in all samples fired at 1400, 1500 and 1600 °C are estimated by Eq. (1) as showed in Fig. 3(a). It is obvious that Mg-α-sialon in final products of samples of $x = 1.2$, 1.4 and 1.6 is quite low, and accompanies with higher content of Si, AlN, and 21R phases compared with those samples whose x value is lower than 1.2 (Fig.3).

All the samples fired at 1500 °C and 1600 °C were bisected and observed by scanning electron microscope (SEM). It was found there were two distinct areas, namely, the dense area at the edge and loose area in the center of the samples of $x = 1.2$, 1.4 and 1.6, and the dense area expanded with x-value of sample compositions. The morphology of a polished surface of $x = 1.6$ sample fired at 1600 °C and its EDS data of dense area and loose area by reduced area collection mode are shown in Fig. 4(a) and Table 1, which is obvious that more N, Mg and Al elements exit at the dense area than at central area. In larger magnification much plate-like grains are easily found in dense area (Fig. 4b), which are confirmed as 21R phases by combining with XRD and EDS. On the contrary a large quantity of recrystal grains of Si are observed in the center area of these samples (Fig.4c). It is suggested that in the early nitridation process metallic Al is nitrided and simultaneously melted into liquid state under 1400 °C, then liquid Al gathers at the edge of sample impelled by the inflation pressure of the sealed gas existing in sample leading to the formation of the dense layer containing Al element at the edge. The presence of dense layer would hinder further nitridation of samples and formation of Mg-α-sialon phase and a large amount of the residual Si is kept in the samples. Higher Al content in samples is, the more remarkable such phenomenon become. It is perhaps the case for the samples of $x = 1.2$, 1.4 and 1.6.

In the previous work, α-sialon had been developed by several researchers using α-Si_3N_4 nuclei [16, 17]; Zhang et al. [8] discovered that α-Si_3N_4 added in the starting composition enhanced the nucleation and growth of Mg-α-sialon grains in the carbothermal reduction and nitridation process. Similar phenomenon was also found in our experiment when the 5% of Si in the starting composition was substituted by Si_3N_4 (α-Si_3N_4 ≥ 90%) according to the principle of not changing the proportion of Si in initial composition. Mg-α-sialon phase in final products all increased in contrast with no Si_3N_4 powder added, especially the samples of $x = 1.2$, 1.4 and 1.6. From XRD patterns of the two samples of $x = 1.2$ (Fig. 5), the content of Mg-α-sialon in samples by adding a small amount of α-Si_3N_4 powder is obviously higher than that in the sample without Si_3N_4 added.

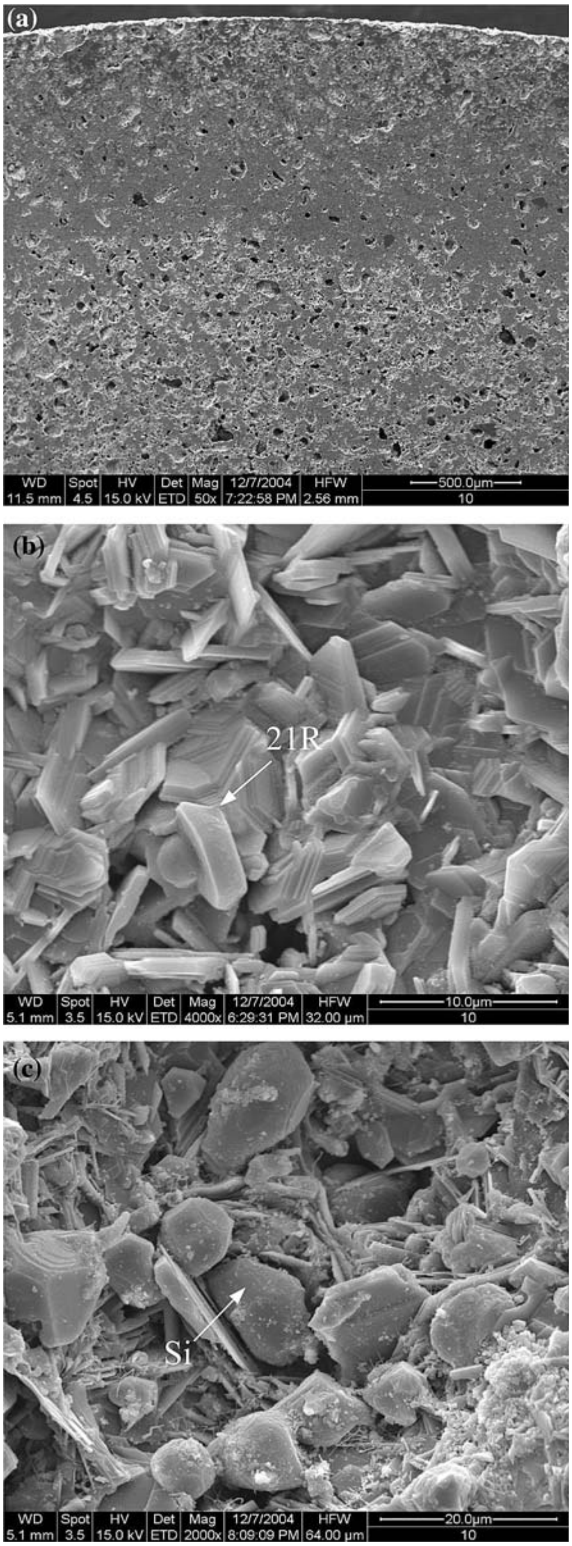


Fig. 4 Morphology of sample $x = 1.6$ fired at 1600 °C

Table 1 EDS data of dense area and loose area

Element	Dense area		Loose area	
	Wt%	At%	Wt%	At%
N	13.21	21.98	12.44	20.64
O	6.72	9.79	7.44	10.80
Mg	5.31	5.15	4.98	4.82
Al	28.09	24.24	25.95	22.33
Si	46.67	38.83	49.9	41.40

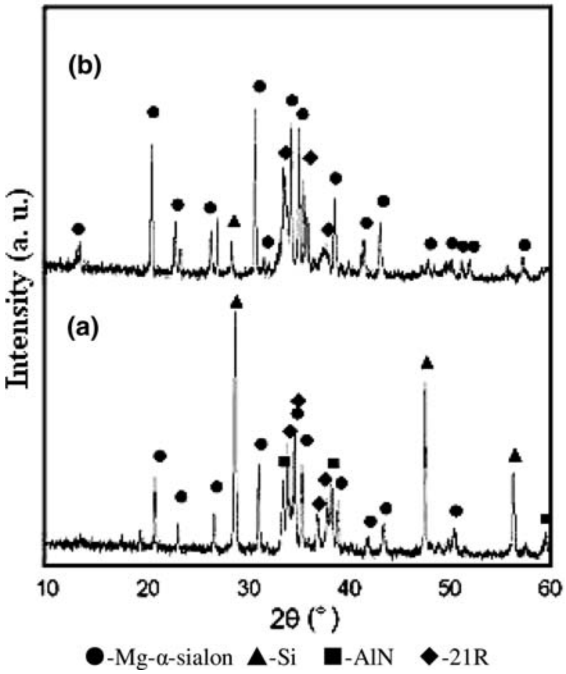


Fig. 5 XRD patterns of $x = 1.2$ samples fired at 1600 °C (**a**) without Si_3N_4 (**b**) with 5% Si_3N_4

Conclusions

Mg-α-sialon was successfully synthesized by using Si, Al and magnesia powders as raw materials in flowing N_2 atmosphere, and greatly dependent of heating temperature and x-value of compositions. Mg-α-sialon phase initially formed at 1400 °C, and increased with elevated temperature in most samples. After the samples of $x = 0.4$, 0.6, 0.8 and 1.0 were nitrided at 1600 °C for 3 h, their final products were mainly composed of Mg-α-sialon phase. In the samples of $x = 1.2$, 1.4 and 1.6, the content of Mg-α-sialon was quite low. However, Mg-α-sialon phase significantly formed in these samples as Si_3N_4 powder was added into the staring mixtures.

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