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Synthesis of (Ca,Mg)-α-sialon from slag by self-propagating high-temperature synthesis

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The synthesis of (Ca,Mg)-α-sialon powders using slag as a starting material by self-propagating high-temperature synthesis (SHS) is reported for the first time. The only crystalline phase detected in the synthesized products was α-sialon. The characters of the synthesized powders were observed and compared with that of conventionally hot-pressed materials. More metal cations were absorbed into the α-sialon structure of the SHS synthesized powders. Fully densified sialon ceramics can be obtained using the SHS powders by hot-pressing. The hardness and fracture toughness of the hot-pressed α-sialon ceramics reached 16 GPa and 5.1 MPa $m^{-1/2}$ respectively.

1 Introduction

Recycling of industrial wastes is gaining more and more attention owing to the ever increasing worldwide consciousness about environmental protection. Slag is a waste product from metallurgical plants and is produced on a daily basis in large quantities. For example, the annual slag production for the Baoshan Steel Company in Shanghai is 2.7×10^7 tonnes. Therefore, there are both economical and ecological reasons to try to reuse the wasteful slag. The basic composition of the slag from a blast furnace contains CaO, SiO_2, Al_2O_3 and MgO. There have previously been attempts to produce cement and glass out of slag.[1,2] However, there is little available in the open literature on the use of slag to synthesize advanced ceramics, although its composition can be easily matched with that of sialon ceramics if extra nitrogen is incorporated.

Sialon ceramics (mainly α-sialon (α′) and β-sialon (β′)) exhibit great potential for engineering applications because of their excellent mechanical properties especially at high temperatures.[3] Typically, sialons are prepared by firing powder compacts of Si_3N_4, AlN, Al_2O_3 and some oxide sintering additives at high temperatures *via* a liquid phase sintering mechanism.[4] Both the expensive starting powders and the complex manufacturing process (compared with most oxide ceramics) have limited the practical application of sialon ceramics. Some researchers have turned to the carbothermal reduction and nitridation (CRN) method to synthesize nitride powders from a wide range of low-cost precursors. There are reports that β-sialon powders have been synthesized by heating mixed clay powders or SiO_2–Al_2O_3 with carbon in flowing nitrogen,[5–7] and α-sialon (α′, $M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$) powders can be made by heating carbon-containing powder mixtures of SiO_2–Al_2O_3–metal compounds or clay–metal compounds in flowing nitrogen.[8] This process requires a high-temperature furnace and long processing times, and hence has obvious disadvantages, such as low-productivity and high-energy consumption.

Recently, a novel synthesis method, namely self-propagating high-temperature synthesis (SHS) has been extensively explored for the preparation of AlN, TiN and $MoSi_2$ powders.[9–11] This technique involves the ignition of a compressed powder mixture, in either air or an inert atmosphere, producing an exothermic chemical reaction, with sufficient heat release so that it becomes self-sustaining. During an SHS process, the temperature may reach several thousand degrees in seconds. The SHS process does not require a high-temperature furnace and the reactions can be completed in seconds instead of hours or days as with the CRN process. Therefore, compared with most conventional synthetic processes, SHS has the advantages of high-productivity and low-energy consumption. Products of high purity can be obtained owing to the vaporization of the volatile contaminants at the extremely high temperatures. The fast cooling in SHS can produce some metastable phases with better sinterability. This last feature makes it especially appealing for the production of α-sialon powders, as α-sialon is known to have poor sinterability. α-Sialon is a solid solution and its composition can be changed in a certain region whilst still maintaining the same α-sialon crystal structure.[12] This flexibility gives special advantages when slag is used for producing α-sialons. As slags from different sources would have different compositions, the compositional fluctuations in the cations could be accommodated by the α-sialon solid solutions. The purpose of this work is to explore the feasibility of synthesizing (Ca,Mg)-α-sialon from slag by SHS. The characteristics of the SHS-synthesized powders and the mechanical properties of the hot-pressed sialon ceramics made from the SHS powders were investigated.

2 Experimental

Slag powder from the Baoshan Steel Company, Shanghai, was used in this work. According to the slag composition (see Table 1) and the Ca–Si–Al–O–N phase relation,[12] the nominal composition of α-sialon was designed as $Ca_{0.71}Mg_{0.23}Si_{9.18}Al_{2.82}O_{0.94}N_{15.06}$, which locates on the tie line between Si_3N_4 and CaO : 3AlN with formula $M_xSi_{12-3x}Al_{3x}O_xN_{16-x}$ ($x = 0.94$). In addition to the slag powders, the starting powders also include Si (Si > 98wt.%, 30 μm), and Al (Al > 98wt.%, 25 μm). Al_2O_3, SiO_2 and other impurity cations in the slag are not considered here in computing the composition. It is therefore expected that some residual phases other than α-sialon may

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Table 1 Chemical composition of the slag from Baoshan Steel Company

Component	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	MnO	TiO_2	SO_3	K_2O	Na_2O	F^-	Cl^-
Wt.%	39.76	34.48	14.04	9.18	0.52	0.09	0.83	1.36	0.25	0.31	0.58	0.27
Mol $(100\ g)^{-1}$	0.71	0.57	0.14	0.23	<0.01	<0.01	0.01	0.02	<0.01	<0.01	0.03	<0.01

exist in the final products. Si_3N_4 and AlN powders were used as seeds or for dilution in the SHS process and were included in the nominal composition of the α-sialon. The mixed powders were put into a graphite crucible and covered with a top layer of titanium powders. A tungsten heating coil was connected to ignite the Ti powder, which then induced the spontaneous SHS process. The whole process was held in a sealed cabin with a high pressure of N_2 and the reaction route can be approximately expressed as:

$$0.71CaO + 0.23MgO + 9.18Si + 2.82Al + 7.53N_2 \rightarrow Ca_{0.71}Mg_{0.23}Si_{9.18}Al_{2.82}O_{0.94}N_{15.06} \quad (1)$$

The resulting powders were attrition milled for 8 h and then hot-pressed in flowing N_2 at 1750 °C for 1 h under a pressure of 20 MPa in a graphite furnace. The bulk densities of the samples were measured according to the Archimedes principle. Phase characterization of the powders was based on X-ray diffraction data from a Guinier-Hägg camera with use of Cu $K\alpha_1$ radiation and Si as an internal standard. The photographs obtained were evaluated with a computerized scanner system.[13] The synthesized α-sialon powder sample was coated with gold and observed under SEM (Hitachi S-570) equipped with EDS (EDAX, Phoenix). An average of ten measurement points on different large grains was used as a representative value of EDS analysis for the samples. The hardness and indentation fracture toughness on the hot-pressed samples were measured using a Vickers diamond indenter under a load of 98 N.

3 Results and discussion

3.1 SHS synthesis of (Ca,Mg)-α-sialon powders

The XRD results (Fig. 1) show that the only crystalline product after SHS is α-sialon, which suggests that the SHS technique may be more suitable for synthesizing α-sialon from impure precursors than the CRN method as the latter often produces β-sialon and other unexpected phases.[8]

Fig. 2 shows a typical curve for combustion temperature *vs.* time.[10] During the SHS process in this work, a tungsten coil is heated for 30–70 s to ignite the Ti powder, and then the Al and Si powders combust violently and react under the high nitrogen pressure. A combustion wave forms and propagates during this process. With reference to the work of Jiang *et al.*[10] on SHS synthesis of AlN, a reaction route can be proposed for the possible mechanisms of (Ca,Mg)-α-sialon powder formation:

$$Si + N_2 \rightarrow Si_3N \quad (2)$$

$$Al + N_2 \rightarrow AlN \quad (3)$$

$$Slag + Si_3N_4 + AlN \rightarrow (Ca,Mg)\text{-}\alpha\text{-sialon} + liquid\ phase \quad (4)$$

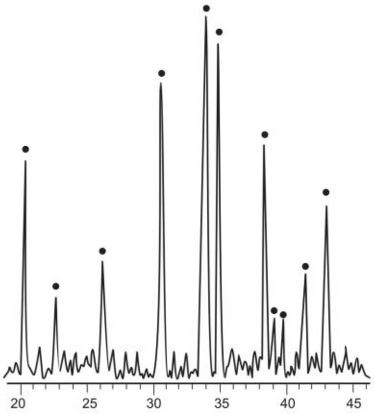

Fig. 1 XRD patterns of powder synthesized by SHS (●, α-sialon).

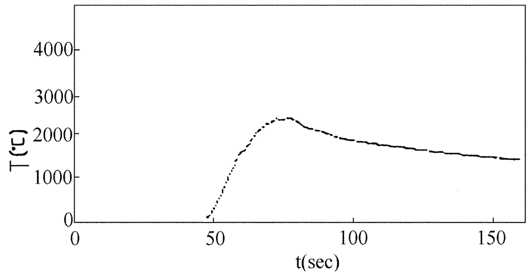

Fig. 2 Typical curve of temperature *vs.* time.[10]

In the initial stages of the SHS reactions the aluminium and silicon powders combust in N_2 and release heat violently [eqns. (2) and (3)]. Then, the slag reacts with the Si_3N_4 and AlN to form the (Ca,Mg)-α-sialon phase [eqn. (4)]. It is thought that synthesis of α-sialon by SHS under a high nitrogen pressure is a complex process and mainly involves thermal explosion, and gas- and liquid-phase reactions. Under different conditions, some of the reactions are more favoured than others. In general, however, because the SHS combustion process yields very high temperatures (above 2000 °C), the reactants involved are in a liquid or gaseous state inside the combustion chamber, which makes the reactions violent and complete in seconds.

3.2 Characteristics of the (Ca,Mg)-α-sialon powder

SHS-synthesized α-sialon powders exhibit non-uniform grain morphologies, as shown in Fig. 3. Some grains have a large

Fig. 3 SEM microstructure of powder synthesized by SHS.

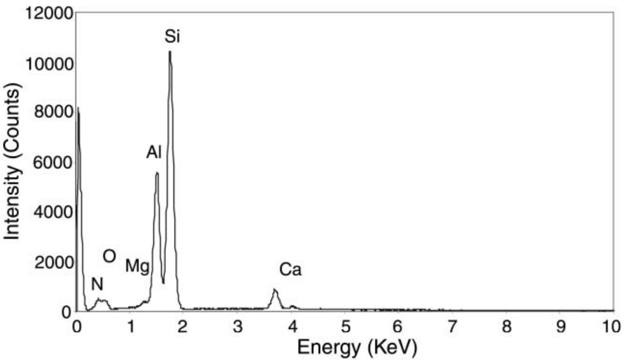

Fig. 4 EDX patterns of (Ca,Mg)-α-sialon composition.

elongated shape and the others show a fine equi-axed morphology. This can be attributed to the complexity of the reactions taken place in a very short time. EDS analysis (see Fig. 4) further supports the XRD results in that both Ca and Mg have been incorporated into the α-sialon structure. Because of the great difference between the SHS synthesis and the more conventional processes, such as hot-pressed and pressureless sintering, it is expected that α-sialon prepared by SHS should have some unique physical and chemical characteristics. This is supported by comparing the phase assembly and α-sialon lattice parameters (Table 2) for the slag-derived sample with those of the hot-pressed samples prepared using Si_3N_4, AlN, $CaCO_3$ and MgO as starting chemicals.[14,15] It has been reported that monolithic (Ca,Mg)-α-sialon is difficult to form in the α-sialon compositions by conventional hot pressing.[14,15] In contrast, no other crystalline phases, such as AlN-polytypoid, appear in the SHS synthesized α-sialon powders. This can be attributed to the higher temperatures and sufficient mass diffusion, which enable more complete reactions for the formation of α-sialon, in the SHS process. The nominal composition of (Ca,Mg)-α-sialon in the present work is x = 0.94; however, based on the results of EDS, the calculated actual x value reaches 0.63. This value is higher than that for a conventionally hot-pressed sample with nominal composition x = 1.0 (Table 3).[14,15] Consequently, the cell volume of α-sialon is also bigger for the SHS-prepared sample. This implies that the α-sialon formed by the SHS process can adsorb more stabilizing cations into its structure. From EDS analysis on the cation concentration (Table 3), a similar conclusion can be drawn for the selective solubility of the different metal cations in the α-sialon lattice, *i.e.*, Ca cations enters into the α-sialon structure more easily than Mg cations.

3.3 Mechanical properties of hot-pressed (Ca,Mg)-α-sialon ceramics

The SHS-synthesized powders were hot-pressed at 1750 °C for 1 h. The density of the sintered sample reaches 3.23 g cm^{-3}, similar to the value for fully dense samples using the normal starting powders. The hardness and toughness, as listed in Table 4, are 16 GPa and 5.1 MPa M$^{-1/2}$, respectively, which are comparable with those of fully dense hot-pressed (Ca,Mg)-α-sialon samples.[15,16] Because α-sialon is the only crystalline phase detected by XRD in the sintered sample, the decrease in hardness must be related to the excessive glass phase (of low hardness, about 10 GPa) at the grain boundary.[8] There are two possible sources leading to the formation of an excessive glass phase in sintered materials: impurities in the starting powders and decomposition of α-sialon in sintering. Therefore, further study is needed to solve these problems before the SHS process can be fully employed in the synthesis of α-sialons.

Table 2 Comparison of phase present and lattice parameters of (Ca,Mg)-α-sialon between SHS-synthesized powders and conventionally hot-pressed materials[14,15]

Nominal x	Ca : Mg (at%)	Phase present[a]	Lattice parameter		
			a/Å	c/Å	V/Å^3
0.6[14]	0.3 : 0.3	α′/s, α/tr	7.7998	5.6650	298.47
0.94	0.71 : 0.23	α′	7.8297	5.6973	302.47
1.0[15]	0.7 : 0.3	α′/s, AlN-polytypoid/mw	7.8286	5.6876	301.80
1.0[14]	0.5 : 0.5	α′/s, AlN-polytypoid/mw	7.8250	5.6853	301.48
1.4[14]	0.7 : 0.7	α′/s, AlN-polytypoid/mw	7.8524	5.7074	304.77

[a] s = strong; m = medium; w = weak; tr = trace.

Table 3 Comparison of actual x of (Ca,Mg)-α-sialon between SHS-synthesized powders and conventional hot-pressed materials[14,15]

Nominal		Actual	
x	Ca : Mg (atom%)	x	Ca : Mg (atom%)
0.6[14]	0.3 : 0.3	0.29	0.25 : 0.04
0.94	0.71 : 0.23	0.63	0.6 : 0.03
1.0[15]	0.7 : 0.3	0.51	—[a]
1.0[14]	0.5 : 0.5	0.5	0.45 : 0.05
1.4[14]	0.7 : 0.7	0.71	0.62 : 0.09

[a] Not measured.

Table 4 Mechanical properties of hot-pressed (Ca,Mg)-α-sialon, at 1750 °C for 1 h, using SHS-synthesized powders and conventional starting powders[15,16]

Nominal x	Density/ g cm^{-3}	Hv_{10}/ GPa	K_{IC}/ MPa m$^{-1/2}$
0.6[16]	3.20	20	5.5
0.94	3.23	16	5.1
1.0[15]	3.21	18	5.4
1.0[16]	3.22	20	5.6
1.4[16]	3.23	18	5.6

4 Conclusion

SHS is a feasible technique for the fabrication of low-cost α-sialon powders from slag. For the composition used in the present work, α-sialon is the only crystalline phase detected in both the final powder and the sintered sample. The SHS method shows some advantage in the formation of α-sialon, with the inclusion of stabilizing cations into the α-sialon structure. Because of the low cost of this process and the starting materials, future applications of the material by industry is therefore anticipated. The hardness and fracture toughness of the hot-pressed sample using SHS-synthesized powders reached 16 GPa and 5.1 MPa M$^{-1/2}$, respectively.

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