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Conversion of Aluminum Dross to Sialon-Based Ceramics by Combustion Synthesis †

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Abstract

Sialon-based ceramics have been synthesized from aluminum dross, which is discharged in aluminum manufacturing, by the nitriding combustion mode of Self-Propagating High Temperature Synthesis (SHS). The Al dross used consisted of mainly AlN, Al_2O_3, and Al. It was blended with the combustion agents of reclaimed Si, and electrically ignited in a pressurized nitrogen atmosphere of 1.0 MPa. The mixtures were converted to sialon phases with a small quantity of unreacted Si. The product powders were sintered at 1500℃ in a nitrogen atmosphere. When the sintered product was heated in air at 1300℃, a mullite layer was formed at the surface with a thickness of 10-15 μm, which could improve significantly the oxidation and corrosion resistance.

KEY WORDS: (Aluminum Dross) (Sialon) (Combustion Synthesis)

1. Introduction

Self-Propagating High Temperature Synthesis (SHS) has a large potential for recycling waste materials because of its high energy efficiency and high reactivity with various compositions.[1] Several investigations on recycling wastes of zinc[2] and radioactive wastes[3] have been reported. We have succeeded in conversing the silicon waste, usually called "silicon sludge", which is discharged in silicon wafer production to sialon-based ceramics by the nitriding combustion mode of SHS.[4] The sintered products showed high chemical stability up to 1000℃. The process requires pressurized nitrogen of 1MPa, but no external heating. The nitriding combustion can be applied to convert other wastes like the aluminum dross as well. Silicon and aluminum powders can be easily reacted with pressurized nitrogen and converted to their nitrides with high reaction temperature up to 2000℃. The formation enthalpies of silicon nitride and aluminum nitride are 740 kJ/mol and 318 kJ/mol at room temperature, respectively. These highly exothermic reactions are effective in the conversion of wastes, including silicon and aluminum, to useful ceramics.

Aluminum dross is discharged during the melting process for casting in aluminum industries. The surface of molten aluminum reacts with air, and Al_2O_3 and AlN are formed. The mixture of such oxides, nitrides, remaining aluminum, and molten salts, which is called 'aluminum dross',[5] is usually buried in the ground, however, there is a fear of generation of harmful NH_3 gas through the hydrolysis reaction of AlN.[6,7] Though the recovery of aluminum and its alloys from the dross was investigated,[8] the cost problem still remains.

In the present study, Al dross was converted to stabilized ceramic powders of sialon by the nitriding

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combustion synthesis. The combustion reaction was conducted in a pressurized nitrogen atmosphere of 1.0 MPa by adding reclaimed Si as a combustion agent. It is important for the conversion to be conducted at a reduced nitrogen pressure, as low as possible, from the economical and safety point of view. The reclaimed Si is a byproduct of silicone production in a chemical industry. The monthly yield of Si is about 250 ton at the Toho Zinc Co. Ltd, Japan. The nitriding combustion reaction was studied by changing the content of the reclaimed Si powder, the nitrogen pressure, and tapping density of reactants. The product was pulverized and sintered. The sintered materials were evaluated for their mechanical, thermal and corrosion resistant properties.

2. Experimental Procedure

The chemical composition of the Al dross, which was supplied by the Toyo Aluminum Co. Ltd., Hino, Japan., was AlN(75 wt.%), Al(12 wt.%), Al_2O_3 (12 wt.%) and a trace of impurities (Fe, V, Ti, Ca, Si, S, C), analyzed by means of X-ray fluorescence analysis and XRD. The lumps of the Al dross were crushed into powders with a mean size of $\leqq 2\,\mu$m by using an iron mortar and vibration milling for 5h. The Al dross was mixed by ball milling for 24h with the reclaimed Si (mean size $\leqq 8\,\mu$m, purity ~93%, Fe 1.1%, Al 0.2%, Ca 0.07%, Toho Zinc Co. Ltd., Yasunaga, Japan) for a combustion agent in different weight ratios of the Al dross /reclaimed Si from 70/30 to 20/80. Figure 1 shows the SHS equipment. The powder mixture of about 35g was charged into a carbon crucible. The reclaimed Al powder, 5.0g of 99.8% purity (Toyo Aluminum Co. Ltd.,) was placed at the bottom of a crucible as an ignition agent. The crucible containing the powders was placed in an autoclave and then pressurized nitrogen was introduced from a nitrogen gas cylinder. The nitriding combustion reaction was initiated by passing a current of ~50 A for several seconds through a carbon ribbon heater which was inserted below the ignition agent.[9] A little decrease in pressure was detected due to the conversion of nitrogen gas to the solid nitrified product. The reaction temperature was measured by a W-Re thermocouple which was protected with a BN spray coating against nitriding. The reaction product phase was identified by XRD.

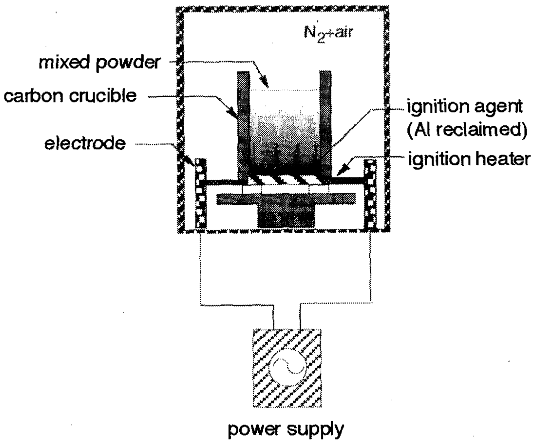


Fig. 1. Autoclave for the combustion synthesis.

The products were pulverized in ethanol for 30 minutes by ball milling, blended with the sintering aids of 3wt.% Al_2O_3 and 3wt.%CaO, vacuum dried, and cold isostatically pressed at 200MPa. The green bodies were sintered at 1500°C for 1-2h in a nitrogen atmosphere. The sintered bodies had a disk shape with a diameter of 26 mm and a thickness of 7 mm. The microstructure of a sintered body was observed by using SEM (JSM-6400). The bulk density was measured by the Archimedes method. Flexural strength was measured for bar specimens of 2×6×23 mm with a cross head speed of 0.5 mm / min and a three-point bending method. Vickers hardness was determined with an indentation load of 19.6N for 10s. The oxidation resistance was evaluated by heating in air at temperatures from 1100°C to 1300°C for 10 hrs, and by thermo gravimetric measurements. The corrosion resistance was examined in NaCl (2N), H_2SO_4 (1N), and NaOH (2N) solutions at room temperature for 25 ~ 200 hrs.

3. Results and Discussion

(1) Nitriding Reaction of Al dross

The combustion reaction of the Al dross with nitrogen was controlled by changing the nitrogen pressure below 1.0 MPa, addition of the reclaimed Si, and tapping density of reactants. The results of the nitriding combustions are shown in Table 1. The combustion reaction could be sustained at 0.6 MPa nitrogen pressure by adding as much as 40 wt.% of the reclaimed Si (sample A40-0.6). However, the reaction was not complete when the content of the reclaimed Si was reduced to 35 wt.% (sample A35-1.0). The combustion reaction lasted about 10 minutes. The maximum combustion temperature at the center of the reactant reached about 1800℃.

XRD patterns of the product powders (A40-1.0, A50-1.0, A70-1.0) depending on the starting compositions are shown in Fig.2. The starting powders were converted completely to sialon phases besides a small quantity of unreacted Si. The sialon phases were identified as $Si_3Al_3O_3N_5$ and $SiAl_4O_2N_4$. These phases correspond to β-sialon ($Si_{6-z}Al_zO_zN_{8-z}$: z=3) with hexagonal structure, and 15R AlN-polytypoid with wurtzite-type structure.[10]

From the reactant and the product phases, the following reactions are considered to take place in this conversion process.

$Al + 0.5N_2 \rightarrow AlN$ (1)
$3Si + 2N_2 \rightarrow Si_3N_4$ (2)
$3Si + 2N_2 + AlN + Al_2O_3 \rightarrow Si_3Al_3O_3N_5$ (3)

The adiabatic combustion temperature should exceed 1500℃ in order to sustain the SHS process.[11] The calculated adiabatic temperature of reaction (3) is about 2200℃. The main reaction of this process are nitriding combustion reactions both of Al and Si shown as reaction (1) and (2). The adiabatic combustion temperatures are 2527℃, and 1927℃, respectively, which are equal to their decomposition temperatures.

Figure 3 shows the composition of the product when the combustion wave was quenched. This product consists of three layers :(A)Combustion zone, (B)Front combustion zone, and (C)unreacted zone. At the front zone, Al was converted to AlN, and the $Si_3Al_3O_3N_5$ phase was observed besides unreacted Si and Al_2O_3. The reaction process is inferred as follows. Firstly, Al reacted with nitrogen and AlN is produced releasing high heat. Next, nitriding of Si occurred and Si_3N_4 is formed. Si could be vaporized at about 1700℃. Si_3N_4 and AlN also have a high vapor pressure at this high temperature

Table 1. Results of the nitriding combustion for Al dross depending on addition of reclaimed Si and nitrogen pressure.

Sample	Reclaimed Si added [wt.%]	Al dross [wt.%]	N_2 pressure (MPa)	Reaction
A80-1.0	80	20	1.0	○
A70-1.0	70	30	1.0	○
A60-1.0	60	40	1.0	○
A50-1.0	50	50	1.0	○
A40-1.0	40	60	1.0	○
A40-0.8	40	60	0.8	○
A40-0.6	40	60	0.6	○
A35-1.0	35	65	1.0	△
A30-1.0	30	70	1.0	×

○reacted △reaction stopped ×not reacted

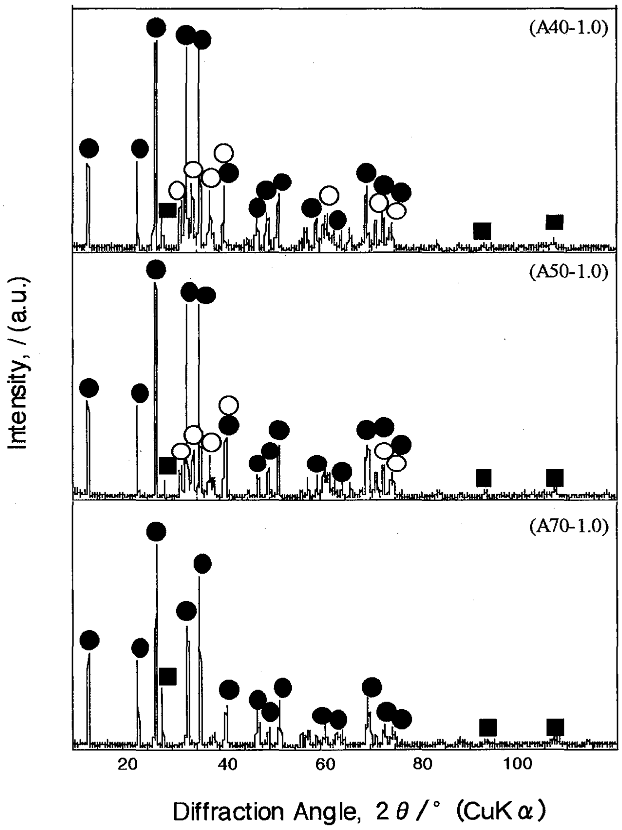
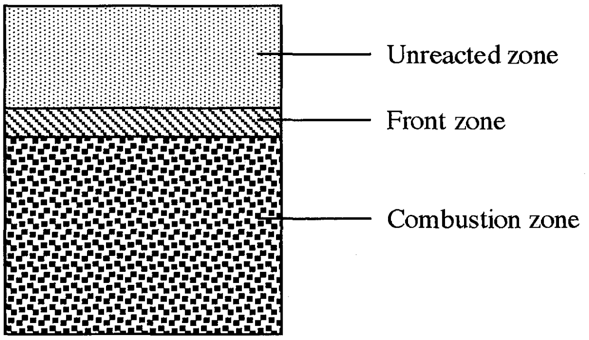


Fig. 2. XRD patterns for product powders for the starting mixtures of A40-1.0, A50-1.0, and A70-1.0.
● : $Si_3Al_3O_3N_5$ ○ : $SiAl_4O_2N_4$ ■ : Si



Not reacted zone	Si, Al, AlN, Al_2O_3
Front zone	Si, AlN, Al_2O_3, β-sialon
Combustion zone	β-sialon

Fig. 3. Composition near the combustion front.

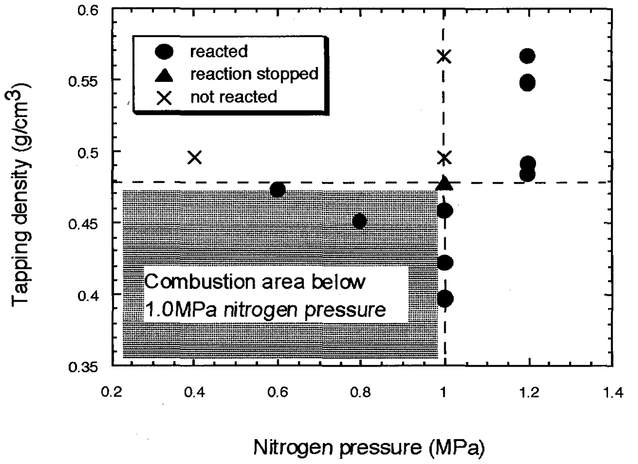


Fig. 4. Reactivity depending on the tapping density of reactants and nitrogen pressures.

region. The vapor phases of Si and Al would promote the reaction with Al_2O_3 and convert it to $Si_3Al_3O_3N_5$. The reactant powder contained excess AlN in comparison with the stoichiometric equation (3). The AlN, Si_3N_4, and Al_2O_3 also formed a small quantity of AlN-polytypoid (15R).

Figure 4 shows the relationship between the tapping density of reactants (dross/Si=60/40 wt.%) and nitrogen pressure against the reactivity. The reactants which have lower tapping density ($\leqq 0.47$ g/cm^3) could sustain the combustion reaction below 1.0MPa. Above the tapping density of 0.47, the nitrogen pressure had to be increased to 1.2 MPa to sustain the reaction. The lower tapping density will provide more reaction area with nitrogen. This result show that the tapping density is an important factor in the nitriding process under lower nitrogen pressure.

(2) Characteristics of sintered products

Mechanical properties of sintered sialon(A40-1.0) are listed in Table 2. The sintered body had a relative density corresponding to 80% of theoretical. A SEM photograph of the surface of the sintered product is shown in Fig. 5. Micro pores are seen at grain boundaries.

The results of the oxidation resistance test for sintered products are shown in Fig. 6. The rate of weight gain increased from 1100℃ to 1200℃, but decreased at 1300℃. Figure 7 are SEM photographs at the surface and the cross section of a sintered sample after heated at 1300℃ in air. Grain growth occurred and an amorphous phase covered the pores. X-ray diffraction showed that a mullite ($2SiO_2 \cdot 3Al_2O_3$) layer was formed at the surface when heated at 1300℃. The thickness of the mullite layer was about 15 μm. Oxynitrides tends to have an oxide layer at the surface after heating in air.[12,13,14] Our results showed that the sintered sialon was covered with the dense mullite layer. Once it is formed at the surface, no oxidation proceeded. Figure 6 (D) showed the sample covered with the mullite layer which was prepared by the post-heat treatment in air at 1300℃ for 5h. These results indicate that the mullite layer is uniformly formed and effective for oxidation protection.

The mullite layer is also effective for corrosive solutions. The corrosion resistance was tested by the weight change in H_2SO_4, NaOH, and NaCl solutions for 200 hours. Figure 8 shows the weight changes of as-sintered and the post-heated samples in each of these solutions. In the case of as-sintered samples, the corrosion weight increased, probably due to the reaction among the sintering aids of CaO-Al_2O_3, residual Al, and the solution at grain boundaries through pores. In contrast,

Table 2. Mechanical properties of sintered samples recycled from aluminum dross (A40-1.0) compared with commercial β - sialon.

	Recycled samples	β -sialon
Density (g/cm^3)	2.5	3.1
Flexural strength (MPa)	110	360
Vickers hardness (GPa)	3.8	15

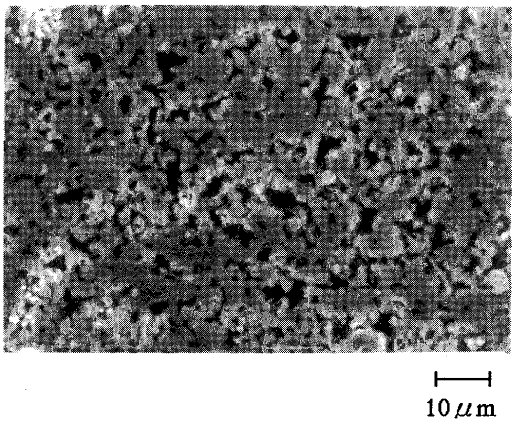


Fig. 5. SEM image of surface of the sintered product (A40-1.0).

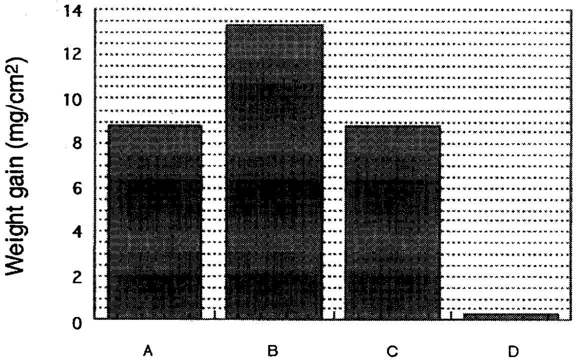


Fig. 6. Results of oxidation test for sintered products.
(A) 1100℃ (B)1200℃ (C)1300℃
(D)1300℃ (Post-heated in air at 1300℃ for 5hs.)

the post-heated sample did not show such weight gain and this can be attributed to the protective function of the mullite layer.

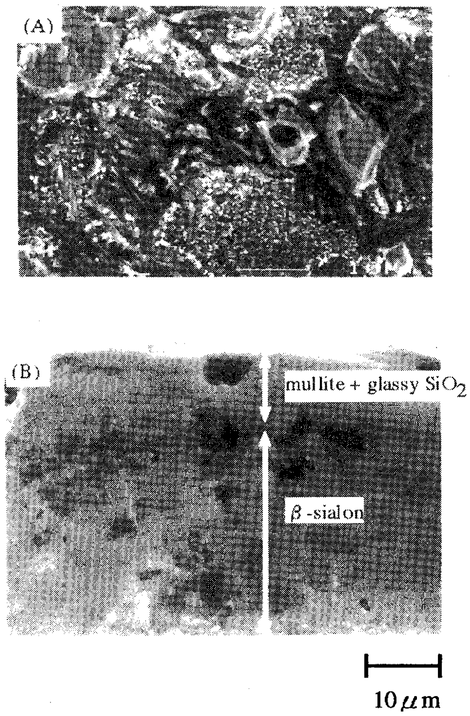


Fig. 7. SEM images of the surface (A) and the cross section (B) of sintered products after the oxidation test at 1300℃.

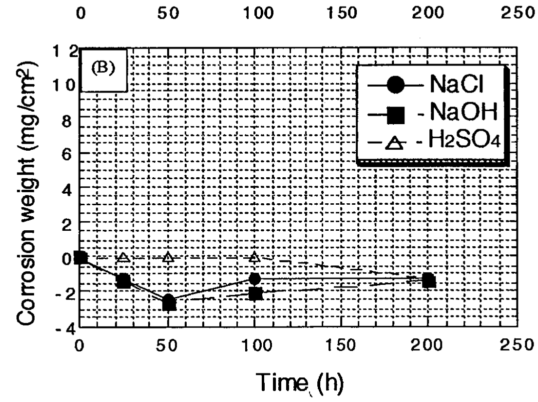


Fig. 8. Changes of corrosion weights of (A)as-sintered products (A40-1.0) (B)post-heated ones at 1300℃ for 5hs as a function of time.

4. Conclusions

An aluminum dross was converted to sialon-based ceramics by means of nitriding combustion of SHS. The results obtained can be summarized as follows.

(1) The aluminum dross must be blended with reclaimed Si to convert it to sialon ceramics under less than 1.0MPa nitrogen atmosphere by nitriding combustion.

(2) The product was mainly β-sialon. The nitriding reaction can be controlled by the addition of reclaimed Si, nitrogen pressure, and tapping density of reactants.

(3) The sialon powders could be sintered at 1500℃ in a nitrogen atmosphere. The sintered sialon was porous with 80 % of theoretical density.

(4) The post-heat treatment for the sintered sialon at 1300℃ in air formed a mullite layer at the surface, which could significantly improve the oxidation and corrosion resistances of the sintered sialon.

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