Combustion Synthesis of Aluminum Nitride From Dross

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For effective use of aluminum dross and development of cost-effective refractory with high thermal conductivity, the combustion synthesis of aluminum nitride was experimentally studied, in which effect of metallic aluminum concentration of a raw material and nitrogen pressure on ignition was mainly examined by using a newly-designed equipment. Once one end of powder mixture of aluminum and alumina was ignited at nitrogen atmosphere, combustion wave of exothermic reaction (AI + 0.5N₂ = AlN) propagated to another end of the powder successfully. With decreasing the aluminum concentration and the nitrogen pressure, the propagating rate decreased. In decreasing the concentration and/or the pressure extremely, it was quite difficult to ignite it. Relationship between nitrogen pressure and aluminum concentration for the possible combustion synthesis of aluminum nitride was expressed in the diagram. This map appealed that aluminum dross can be a raw material of the combustion synthesis for producing aluminum nitride industrially by controlling the conditions.

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1. Introduction

The aluminum industry has been recently emitting a huge amount of waste material; so-called aluminum dross. The aluminum dross shall consist of slag, dross, skimming, and spilling from aluminum melting operations. In particular, its amount reaches as much as 350000 ton per year in Japan,¹ causing a serious social problem of air and water pollution with a bad smell because the dross left outside reacts easily with water to emit harmful gas such as hydrogen sulfide, methane and ammonia. In addition, we always suffer from lack of places for the interment. To avoid such problem, the dross is usually thermally decomposed. However, since this treatment is energy-consuming, requesting as much as $200 to 300 per ton,¹ the solution of this problem is strongly and urgently requested from a social aspect.

In contrast, aluminum-nitride-based material has been focused³ as heat sink, refractory, structural materials, etc., due to high thermal conductivity, low thermal expansion and low density. For producing this material, the combustion synthesis is attractive,³-⁶ in which aluminum nitride is normally combustion-synthesized from pure aluminum, not wasted aluminum. In general, the combustion synthesis offers many benefits; (1) low energy requirement, (2) short processing time, (3) simple equipment, (4) high pure product, and (5) direct synthesis of metal hydride,⁷-¹⁹ etc. In this process, once one end of aluminum powder is ignited at highly pressurized nitrogen atmosphere, self-propagating reaction between aluminum and nitrogen occurs due to largely exothermic heat. All phenomena of the combustion synthesis; its ignition, heat wave propagation and completion, is easily predicted to be influenced by a process parameter such as aluminum impurity and nitrogen pressure. However, effect of such conditions on the combustion synthesis is not well explained yet in spite of its significance.

The dross has not been almost regarded as a raw material of the combustion synthesis except some reports²⁰,²¹ because it is essentially treated as an industrial waste, although having 10 to 60 mass% in metallic aluminum. To solve these problems, this fundamental study was planned and carried out. Thus, the purpose of this paper is to investigate experimentally a possibility of a new aluminum-nitride synthesis process, in which effect of aluminum concentration of a raw material and nitrogen pressure on ignition was mainly examined by using newly-designed equipment. The results obtained will give valuable information on the possible operating conditions. It will enhance effective use of aluminum-containing waste to produce aluminum nitride by the combustion synthesis. This technology will also promote a recycling system by reducing waste and using it as a raw material for another process.

2. Sample

Industrially discharged aluminum dross contains still 10 to 60% in metallic aluminum and its shape is like powder or strip. Its main components are aluminum and alumina, with a small amount of aluminum nitride. Based on this fact, the mixture of metallic aluminum and alumina powders were prepared as a sample, in which pure aluminum powder; 99.8 mass% in purity and 59.7 µm in average dimension, was mainly employed. In addition, to study influence of impurity of a raw material, alumina powder; less than 100 µm in dimension, was added to the aluminum powder by 0 to 80% in weight.

Sample preparation procedure was that aluminum powder was first well mixed with alumina in liquid acetone by a glass bar until complete drying of the acetone, and then placed in the below-mentioned container without any compressive treatment. This is a unique point of the equipment used in this study. Until now, the sample was usually located longitudinally and top or bottom of the sample was ignited in the conventional combustion synthesis process, in which the
compressive treatment of the sample was a must. Figure 1 shows a schematic diagram of the sample container, which was made from commercially available iron angle with triangle shape. The iron was cut to be the desired length; 120 to 130 mm, then it was covered with an alumina paper as thermal insulation. Weight of the aluminum sample with/without alumina was approximately 22 g and its void fraction of the sample bed was 41%. As an igniter, disposable carbon foil; 8 mm \( \times \) 135 mm \( \times \) 0.1 mm, was contacted to one end of the sample bed and was electrically-flashed by a power of 40 V and 70 mA in the experiments.

3. Method

Figure 2 shows a schematic diagram of the experimental apparatus. It consists of the three parts; a pressure-resistance reactor, gas supply system and vacuum system. Maximum pressure of this reactor is 1.0 MPa. After the sample container was placed in the reactor, a rotary pump (R.P.) evacuated up to 13.3 Pa (0.1 Torr), then pure nitrogen was supplied and finally one end of the sample was instantaneously heated by using the carbon foil. In the experiments, nitrogen pressure ranged between 0.2 and 1.0 MPa in the interval of 0.2 MPa, for examining its effect on the product. During the experiment, pressure was kept constant by supplying gas.

It is well known that heat wave starts to propagate horizontally without any additional energy shortly after the ignition. This phenomenon is simply explained by the following exothermic reaction;

\[
\text{Al} + 0.5\text{N}_2 \rightarrow \text{AlN}, \quad \Delta H_{298} = -318 \text{kJ/mol}
\]

All phenomena during the combustion synthesis; namely, ignition, propagation and completion, was observed through upper and side quartz windows of the apparatus and was recordable by a video camera. The total processing time for wave propagation from one end to another was also measured. From this value and length of the sample, an average propagating rate was calculated. Strictly speaking, the propagation rate is not constant due to the end effect, in which heat loss in the end makes slower. However, its effect was neglected because the sample length was relatively long and the value of average rate was enough for comparing the influence of experimental conditions on the propagation phenomena of heat wave. When the frame vanished before another end of the sample, its actually propagated distance was measured. After being cooled down completely, the product was taken out at laterally different positions, identified by X-ray diffraction analysis (XRD) and observed by Scanning Electron Microscope (SEM). Preliminary tests using aluminum with different size from 50 to 200 \( \mu \)m in average showed that the size effect on the total processing time was negligible under this condition.

4. Results and Discussions

We confirmed that once one end of the sample was ignited, the combustion wave slowly propagated to another end, emitting much light and smoke. Figure 3 shows the experimental results obtained at different nitrogen pressures. The results showed that the propagating rate became slow gradually with decreasing nitrogen pressure, as expected. For example, the propagating time was only 60 s under the pressure condition of 0.9 MPa and as much as 190 s, 0.3 MPa. Very significantly, the condition of only 0.3 MPa nitrogen pressure was able to complete the combustion synthesis of alumina nitride. When nitrogen pressure was less than 0.3 MPa, the sample was not ignited or the combustion wave did not advance due to extinction even if it was ignited.

In contrast, Fig. 4 shows the relationship between the propagating time and the ratio of alumina to metallic aluminum. Interestingly, with adding alumina to metallic aluminum, the propagation rate of combustion wave became slower due to dilution effect. For example, 5% alumina addition to aluminum took approximately 200 s for the synthesis completion, and 40% addition, 550 s. Moreover, a very small amount of alumina addition to aluminum decelerated the propagation rate drastically, in comparison to the combustion synthesis from pure aluminum.

In addition, the rough observation of cross-sectional area of samples after the reaction was interesting. It was easily realized that the sample was melt by large heat of reaction during the experiment. This result means that the nitriding reaction proceeds with melting of alumina, not in the solid phase.
Figures 5 and 6 show the XRD patterns of the products, collected near the ignited place. Obviously, nitrogen pressure influenced on purity of the product very much. That is; when over 0.4 MPa of nitrogen pressure as operating conditions, the samples changed completely to pure aluminum nitride from pure aluminum. In contrast, un-reacted aluminum was observed at the lower pressure conditions, when extinction or non-ignition phenomena was found. That is; the sample did not react with nitrogen at all under the conditions of 0.2 MPa in pressure. Under the condition of 0.25 MPa, the ignition and the heat wave propagation were observed in fact, however the heat wave did not reach another end of the sample due to extinction. Figure 7 shows microscopic view of the product synthesized under the conditions of 0.8 MPa in pressure when pure aluminum was used as a raw material. The product was particulate with rough shape, in which the dimension ranged from 1 to 5 μm. The dimension of the product was slightly influenced by pressure conditions, however any products were particulate shape.

Forty-seven experiments of the combustion synthesis were conducted using chemicals, not real dross, and then the results were schematically summarized. All experimental data were plotted and drawn by contour, as shown in Fig. 8, on the diagram of aluminum concentration and nitrogen pressure. Here, dimensionless distance value of the combustion wave propagation; actual propagated distance/sample length, was employed for simple evaluation. The value of one means the propagation completion and zero, no ignition. At the case of
Fig. 8 Obtained operating map for the combustion synthesis of AlN at different pressures and aluminum/alumina ratios, in which the right upper (red) zone means successful synthesis conditions.

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<th>Table 1 Chemical compositions of the aluminum dross* used.</th>
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<td>MAl</td>
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*Trace value; Na, K, Ti, F, Fe

extinction, it takes a value between zero and one. As a result, right upper (dark) area of this diagram demonstrates clearly the possible operating zone for completing reaction. This diagram shows us available nitrogen pressure under the given condition of metallic aluminum concentration in a raw material. For validating this operating map, the real aluminum dross, as listed in Table 1, was ignited after drying, under the same procedure of the experiment mentioned before. The size of the dross used ranged from 10 to 50 mm; its shape was irregular, like powder and string. When a raw material needs over 60% in aluminum concentration, pure aluminum powder was added to the real dross. In Fig. 8, circle, triangle and cross mean complete propagation, extinction and no ignition, respectively. Most significantly, all of the plotted data agreed with the map without any exception, and it demonstrated satisfactory validation of the map. This also means that the ignition and propagation conditions of this phenomena do not depend on the size and shape of raw material.

5. Conclusion

In order to produce aluminum nitride from aluminum-containing industrial waste such as dross, effect of metallic aluminum concentration of a raw material and nitrogen pressure on the combustion synthesis was systematically examined and then revealed. The obtained, operating map showed clearly the relationship between nitrogen pressure and aluminum concentration for the combustion synthesis of aluminum nitride. The results also showed that a possibility of the combustion synthesis depended significantly on the combination of the conditions. Propagating rate of the combustion wave became larger with higher nitrogen pressure and more aluminum concentration. The map appealed that aluminum dross can be a raw material of the combustion synthesis for producing aluminum nitride industrially by controlling the conditions. The powder obtained from the dross; mixture of alumina and aluminum nitride, could be used as a high temperature refractory with high thermal conductivity.

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REFERENCES