Preparation and Characterization of Core-Shell Al/Al₂O₃ Composites with Adjusted Structure through Fast Hydrothermal Oxidation of Aluminum

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Abstract. A method for preparation of core-shell Al/Al₂O₃ composites with adjusted structure was proposed. It was based on two steps: fast hydrothermal partial oxidation of aluminum in continuous reactor and subsequent thermal treatment in muffle furnace to convert aluminum hydroxide to γ-Al₂O₃. It was shown the possibility to create metal-ceramic composites with adjustable content of metallic core by temperature of hydrothermal process. During experimental study it was established that oxidation degree for aluminum powder with average size of 22 μm was changed from 40 to almost 100 % when temperature in hydrothermal reactor changed from 280 to 350 °C. The reaction time was no more than 10 min. Obtained products were studied by scanning electron microscopy, pore structure analysis and XRD analysis. Prepared core-shell Al/γ-Al₂O₃ composites can be used as catalyst materials as well as for additive technologies.

1. Introduction

The production of micro- and nano-structured metal oxides or composites with specific structure, shape and morphology have attracted a great attention in recent years due to the necessity of such materials in fabrication of ceramics, adsorbents, filters and catalyst carriers. Due to unique properties of such materials they can be used also in different areas such as optical and semiconductor industry, quantum electronics, electric-power industry, instrument engineering, etc. [1-2, 14-15].

One of simple way to produce Al/Al₂O₃ composites is aluminum oxidation in water or aqueous solutions. An interest in this process is due to the high chemical activity of highly dispersed aluminum powders in the reactions with water or water vapor. The use of pure water as an oxidant in its reaction with dispersed aluminum makes it possible to synthesize high purity hydrogen, a large amount of high temperature steam, and a variety of aluminum hydroxides [3-4]. The main element of the units for hydrothermal oxidation of aluminum by water or steam is a reactor that generates also a steam-hydrogen mixture, that can be used as a working medium of conventional and future heat engines and generators [5-6]. Usually reactor represents an autoclave and in case of aluminum oxidation it operates during several hours [7-10].

One of the promising methods of advanced materials production is hydrothermal processing. The term hydrothermal technology covers the broad spectrum of different techniques [11] and commonly it implies the use of aqueous solutions at elevated temperatures (> 100 °C) and pressures (> 0.1 MPa). The success in advanced materials production under hydrothermal conditions is usually bound up with unique properties (density, viscosity, ionic product, dielectric constant etc.) of water at elevated thermodynamic parameters [11].
A way of advanced alumina or alumina-aluminum composites production is hydrothermal oxidation of aluminum. The reaction of aluminum oxidation by water, generally, can be realized in the following ways:

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\begin{align*}
\text{Al} + 3\text{H}_2\text{O} &\rightarrow 0.5\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O} + 1.5\text{H}_2 + 427.98 \text{ kJ/mole}, \\
\text{Al} + 2\text{H}_2\text{O} &\rightarrow 0.5\text{Al}_2\text{O}_3\cdot \text{H}_2\text{O} + 1.5\text{H}_2 + 415.24 \text{ kJ/mole}, \\
\text{Al} + 1.5\text{H}_2\text{O} &\rightarrow 0.5\text{Al}_2\text{O}_3 + 1.5\text{H}_2 + 407.7 \text{ kJ/mole}.
\end{align*}
\]

Channel (1) prevails at temperature up to 200 °C, (2) prevails in the field of 200÷400 °C and further temperature increase leads to \(\text{Al}_2\text{O}_3\) formation (channel (3)).

Some attempts to produce advanced materials by hydrothermal oxidation of aluminum have been already carried out. Main factors that influence on both reaction kinetics and physicochemical properties of solid products of hydrothermal oxidation of aluminum are thermodynamic conditions, initial surface area of aluminum and technological conditions.

Low temperature (about 100 °C) hydrothermal oxidation of aluminum micron powder in batch reactor and subsequent thermal dehydration were proposed for the synthesis of porous \(\text{Al}_2\text{O}_3/\text{Al}\) composites (cermets) in [7]. Hydrothermal oxidation was carried out in open bucket under intensive mixing. The duration of hydrothermal treatment was from 1 to 5 hours. Although produced composites possessed high surface area (about 30-40 m²/g) and advanced porous structure, the conversion degree of aluminum didn’t exceed 60 %. In [12] it was shown that reaction can be promoted by applying the ultrasonic activation influencing also on product structure. It was shown that ultrasonic field promotes the aluminum micron particles dispersion into microcrystallites during oxidation process.

In [9] the product synthesized by hydrothermal oxidation of aluminum in autoclave at 250 °C was also used for \(\text{Al}_2\text{O}_3/\text{Al}\) composite production. Aluminum was used in the form of micron powder as well. Autoclave was heated to 250 °C during 40 min and then was maintained heated for 6.5 hours. The products of hydrothermal oxidation were dried and calcined at temperatures of 520 °C for 2 hours. After calcination the content of oxide in the sample was about 37 wt.%. Following the study of pore structure of synthesized \(\text{Al}_2\text{O}_3/\text{Al}\) composite it was established that the product has high surface area (about 60 m²/g) and narrow pore size distribution and can be viewed as promising material in catalysis and adsorption.

In present work hydrothermal oxidation of aluminum micron powder was carried out under 240-350 °C in a flow reactor for fast up to 10-min aluminum oxidation. Main object of this study was the investigation of structural properties of \(\text{Al}/\text{Al}_2\text{O}_3\) composites obtained.

2. Materials and Methods

Hydrothermal oxidation of aluminum powder was carried out on experimental plant designed generally for energy application [13]. Deionized water and micron powder of aluminum were used as starting reagents. Aluminum powder used in experiments was purchased from Rusal. Powder represents spherical particles with average size of about 22 μm.

The synthesis of \(\text{Al}/\text{Al}_2\text{O}_3\) composites at different temperatures was performed during the series of model experiments. Mixture of aluminum powder with water was prepared at room temperature within mixing tank. Then small portion of mixture containing about 50 g of Al was injected by high-pressure dosage pump into preliminary heated 7.5 l reactor. After 10 minutes the mixture of oxidation product and water was withdrawn from the reactor.

Solid product produced by aluminum hydrothermal oxidation at different temperatures were separately dried and analyzed by scanning electron microscopy, X-ray analysis, analysis of specific surface, analysis of pore structure and mass spectrometry.

Surface morphology of solid products was studied on JEOL JSM-7401F scanning electron microscope (SEM). Samples were placed into the microscope on carbon substrate. The shooting was carried out at 1 kV accelerating voltage. Samples were studied at the magnification in the range of 100-200000. Phase composition of oxidation product was studied by X-ray diffraction (XRD) using Thermo ARL XTRA diffractometer using CuKα radiation (\(\lambda=0.15418 \text{ nm}\)). The specific surface of
product was studied by low-temperature nitrogen adsorption using Sorbi 4.1 device. For thermal treatment a muffle furnace LHT 08/16 (Nabertherm) was used.

3. Results and Discussion

Table 1 shows the results of experiments of aluminum oxidation. It can be seen that by temperature adjustment we can achieve specific oxidation degree. For total oxidation of aluminum powder with the size of 22 μm temperature should be more than 350 °C. Temperature decreasing lead to the aluminum conversion decreasing (at one time of staying inside the reactor – 10 min). At 280 °C aluminum conversion after 10 min oxidation decreased to about 40 % thus producing Al/Al₂O₃ composite.

Table 1. Results of hydrothermal oxidation of aluminum powder with the size of 22 μm.

| Reaction temperature, °C | Reaction pressure, MPa | Aluminum conversion degree, % |
|--------------------------|------------------------|-------------------------------|
| 350                      | 16.1                   | 100                           |
| 332                      | 12.8                   | 91                            |
| 316                      | 10.5                   | 86                            |
| 280                      | 6.8                    | 40                            |

Fig. 1 shows SEM images of initial aluminum particle and solid oxidation product. It can be seen that the surface of aluminum is covered by dense aluminum hydroxide layer. Fig. 2 with larger magnification show that the size of single crystal is changed from several nanometers to hundreds nanometers.

Figure 1. SEM images of initial aluminum powder and oxidation product.

X-ray analysis of oxidation product showed that the product of hydrothermal oxidation of aluminum in the range of 240-350 °C is aluminum oxyhydroxide – boehmite (γ-AlOOH). Fig. 3 shows the XRD plot for oxidation product obtained at 316 °C. All peaks on XRD plot correspond to AlOOH and just one intensive peak corresponds to non-oxidized aluminum core. The calculation of coherent scattering area for boehmite crystals produced by hydrothermal oxidation of aluminum showed that temperature increasing leads to the increasing of size of boehmite crystals.

It is important to note that although thermodynamic parameters and size of aluminum particles were the same as in previous studies with autoclave the conversion degree in case of flow reactor was turned out to be higher. For example in [7, 9] in autoclave hydrothermal conditions at 250 °C the conversion degree was less than 30 % after 6.5 hours treatment. In our work we achieved 40 % at 240 °C after 10 min oxidation. During the slow heating of autoclave the surface of aluminum in hydrothermal conditions is covered by dense layer of hydroxide. By the time when autoclave reaches maximum temperature aluminum particle has already partially oxidized and covered by oxidation product microporous layer whose thickness is several times more than the thickness of initial oxide.
film covered aluminum particles. This layer is certain to complicate the diffusion of water to the surface of unreacted aluminum core and thus reducing the rate of chemical reaction. When aluminum particles come into already heated flow reactor the micron sized aluminum core is shock heated to nominal temperature by less than a second. Such shock heating expands the aluminum core and splits the oxide film on the surface of aluminum thus practically eliminating the induction period. Reaction starts immediately. Thus in flow reactor the conversion degree of aluminum is improved in comparison with autoclave method.

Fig. 4 shows SEM surface of Al/AlOOH composite produced at 280 °C and the product of its thermal treatment in muffle furnace at temperature of 650 °C. At this temperature the boehmite (AlOOH) was transformed into γ-Al₂O₃. It can be seen that the structure of the surface is changed. Due to thermal treatment the size of crystal becomes smaller. It can be explained by the loss of crystallized water. The surface of oxidation product at 280 °C was 58.9 m²/g, the surface of the product after thermal treatment at 650 °C was 80.2 m²/g.

**4. Conclusion**
The results of the study confirmed in general that hydrothermal oxidation of aluminum is a promising method of production of Al/Al₂O₃ or Al/AlOOH composites. It is important to note that by proposed method it is possible to adjust the size of core and shell by reaction temperature.
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