Kinetics of Aluminum Micron Powder Oxidation in Hot Distilled Water and Product Microstructure Investigation

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Abstract. The kinetics of aluminium oxidation by distilled water in batch type reactor (autoclave) in temperature range of 100-200 °C and product microstructure was studied. The product in presented work represents Al/γ-Al2O3 composite obtained after autoclave oxidation, drying (at 120 °C) and calcination (at 600 °C).

1. Introduction
Recently the Al/Al2O3 has attracted considerable attention as perspective material for many potential applications in aerospace, defense, constructional and automotive industries [1-2]. One of simple ways to produce Al/Al2O3 composites is aluminum oxidation in water or aqueous solutions. 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 porous aluminum hydroxides [3-4] as well as high purity alumina [5-7]. The main element of the plant 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 [8-10].

In our previous work we proposed a method for preparation of Al/Al2O3 composites by two steps [11]: 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 22μm was changed from 40 to almost 100 % when temperature in hydrothermal reactor changed from 280 to 350°C. The reaction time was about several minutes.

In present work we concentrated on low and medium temperature oxidation. In our previous study [4] it was shown that temperature increasing leads to less-ordered structure, particle agglomeration increasing, average crystal size increasing, specific surface decreasing, micropore volume decreasing and mesopore and macropore volumes increasing. In present work we study the kinetics of aluminum oxidation in distilled water in batch type reactor in temperature range of 100-200 °C and product microstructure.

2. Experimental
Oxidation of aluminum powder was carried out on experimental plant shown in fig.1. Deionized water and micron powder of aluminum (Rusal) were used as starting reagents. Powder represents spherical particles with average size of about 40μm.
Figure 1. Scheme of the autoclave: 1 – Overhead stirrer, 2 – Reactor autoclave, 3 – Bubbler, 4 – The gas drum counter, 5 – Heat exchanger, 6 – Distilled water storage tank, 7 – Magnetic coupling with cooling circuit, 8 – Funnel for aluminum backfilling and for water filling, 9 – Product acceptance tank, M – Manometer, F – Filter, Vs – Adjustable safety valve, T – Thermocouple, V1-8 – Valves.

Al/Al₂O₃ composites were prepared in five different regimes. The parameters of these regimes are shown in table 1. In the A regime the suspension from 1 kg of aluminum and 0.5 kg of water was prepared and mixed, than aluminum was decanted and the excess of water (about 0.15 kg) was deleted, and then such “wet” aluminum powder was dried. In A regime aluminum was not loaded and heated in autoclave. In this case aluminum was oxidized during mostly the drying. The calcination of oxidation product at 600°C led to the transformation of aluminum hydroxides into aluminum oxide (γ-Al₂O₃). In regimes B-E autoclave oxidation stage parameters were different (see table 1). In all experiments the temperature of drying and temperature of calcinations were the same and equaled to 120 and 600°C respectively.

Solid products produced in different regimes were separately dried and analyzed by aluminum oxidation degree evaluation, scanning electron microscopy and X-ray analysis.

Aluminum oxidation degree evaluation was carried out on experimental plant described in [12-13]. That experimental plant was based on glass reactor with stirring and gas flow meter. Aluminum was loaded into 0.1 M KOH aqueous solution and the yield of hydrogen was precisely measured. Aluminum oxidation degree was calculated from the yield of hydrogen. The error in aluminum oxidation degree evaluation was no more than 1%.

Surface morphology of solid products was studied on JEOL JSM-7401F scanning electron microscope (SEM). Phase composition of oxidation product was studied by X-ray diffraction (XRD) using DRON-2 (USSR). For thermal treatment a muffle furnace LHT 08/16 (Nabertherm) was used.
Table 1. Parameters of experiments in which the Al/Al₂O₃ composites were prepared

| Regime | Suspension composition | Maximum heating temperature, °C | Maximum pressure, bar | Volume of H₂ formed in the autoclave and passed through the gas drum counter, l | Temperature of drying, °C | Temperature of calcination, °C |
|--------|------------------------|-------------------------------|----------------------|----------------------------------|--------------------------|-------------------------------|
| A      | 1 kg of aluminum and 0.5 kg of water | -                             | -                    | -                                | 120                       | 600                           |
| B      | 1 kg of aluminum and 3 kg of water | 120                           | 0.5                  | 65                               | 120                       | 600                           |
| C      | 1.5 kg of aluminum and 2.8 kg of water | 180                           | 12.5                 | 190                              | 120                       | 600                           |
| D      | 1.5 kg of aluminum and 2.8 kg of water | 190                           | 14                   | 260                              | 120                       | 600                           |
| E      | 1.5 kg of aluminum and 2.8 kg of water | 200                           | 17                   | 300                              | 120                       | 600                           |

3. Results and discussion
The Fig. 2-5 shows the autoclaves parameters in experiments in regimes B-E. It can be seen that in all experiments reaction of aluminum oxidation in distilled water starts at about 68 °C. It can be explained by partial permeability of an oxide layer and decreasing of water viscosity with temperature increasing. Temperature increasing lead to the increasing of volume of hydrogen formed in the autoclave and passed through the gas drum counter before the cooling of the autoclave began. It should be noted that this volume of hydrogen cannot be used for aluminum oxidation degree evaluation because of several reasons. At first, some unknown amount of hydrogen remained in the autoclave and other vessels, and at second, aluminum continues oxidation during the drying and calcinations. Aluminum oxidation degree evaluation in Al/Al₂O₃ composites should be carried out separately after the drying and calcination.
Figure 2. Parameters of experiment in B regime

Figure 3. Parameters of experiment in C regime

Table 2 shows the results of aluminum oxidation degree evaluation for experiments in regimes A-E. It can be seen that even without autoclave oxidation the product (after the drying of “wet” aluminum powder) was oxidized by 5.5 %. Relatively simple and fast regime B gives 10.9 % oxidation degree. Further temperature and duration (reaction time) increasing lead to the increasing of oxidation degree. In regime E at maximum temperature of 200 °C and about 2 h reaction time the oxidation degree was 21.3 %.
Temperature and duration (reaction time) increasing lead to the change of microstructure of Al/Al2O3 composites. Fig. 6 shows the product in regime A. It is seen that the particles did not change their spherical shape as a result of oxidation. The micrographs show that the aluminum surface was covered with a layer of aluminum oxide and the oxide layer covering the granules is about 400 nm thick. With further magnification, it can be seen that the resulting oxide layer is an irregular "petal" structure formed from alumina crystals. The thickness of the elements making up this structure is about 6 nm.
Figure 6. Micrographs of the product in regime A

In contrast to the sample with a degree of oxidation of 5.5% in a sample with a degree of oxidation of 10.9%, relatively large crystals were also observed on the surface of aluminum particles in addition to the "petals" (fig. 7). Crystal growth accelerates with temperature increasing. With increasing residence time of aluminum particles in the autoclave (reaction time), these crystals become larger. This can be explained by the local dissolution of the "petals" and by the crystallization of the hydroxide on the nuclei. It can be noted that an increase in the degree of oxidation of the aluminum powder occurred together with the coarsening of the alumina crystals.

Fig. 8 shows the product in regime E. It shows that a relatively smooth surface of aluminum powder was covered with a layer of aluminum oxide. It shows that the oxide layer covering the aluminum granules is about 1000 nm. The layer of aluminum oxide consists of crystals with a size of several hundred nm. It is also seen that a small part of the alumina is detached from the surface and it is present in the product as individual fine alumina particles. It has been experimentally established that the amount of aluminum oxide that has broken off from the surface of the spherical particles increases with the duration of the autoclave oxidation process.

| Table 2. Results of aluminum oxidation degree evaluation for experiments in regimes A-E |
|----------------------------------|---|---|---|---|---|
| Regime | A | B | C | D | E |
| Oxidation degree, % | 5.5 | 10.9 | 14.5 | 17.4 | 21.3 |
Figure 7. Micrographs of the product in regime B

Figure 8. Micrographs of the product in regime E
4. Conclusion
The kinetics of aluminum oxidation by distilled water in batch type reactor (autoclave) in temperature range of 100-200°C and product microstructure was studied. The product in presented work represents Al/Al2O3 composite obtained after autoclave oxidation, drying (at 120°C) and calcination (at 600°C). It was shown that aluminum oxidation degree change from 5.5 % for experiment in which wet aluminum powder was just dried and calcined (i.e. without autoclave stage) up to 21.3 % for experiment with maximum autoclave temperature of 200°C and about 2 h reaction time. The thickness of porous alumina layer on the surface of aluminum increased with oxidation degree (reaction temperature and duration) increasing. At about 100°C oxidation temperature the thickness of the layer is about 300-400 nm and at 200°C the thickness is about 1000 nm. The size of single crystal changes from about 6 nm to 200-300 nm.

5. References
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