Synthesis of core-shell Al/Al$_2$O$_3$ composite through aluminum powder oxidation in hot water and its characterization

G N Ambaryan*, M S Vlaskin, E I Shkolnikov and A Z Zhuk
Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia
E-mail: ambaryan1991@gmail.com

Abstract. Simple and potentially energy efficient way for synthesis of Al/Al$_2$O$_3$ composites is described. Synthesis method is based on aluminum powder oxidation in water at 100-200 °C and following drying and calcination at 600 °C. Aluminum powder with average size of about 40 μm that is currently applied in additive manufacturing was used. Present work was devoted to the study of oxidation degree of aluminum and so the propagation depth and structure of Al$_2$O$_3$ shell in composite’s matrix. Al/Al$_2$O$_3$ composites were produced in different regimes with different maximum temperature and duration of the process of aluminium oxidation in water. Aluminum oxidation degree and aluminium content in obtained Al/Al$_2$O$_3$ were changed in the range from 5.5 % and 90.1 % to 21.3 % and 66.2 % respectively. The size of single crystals of Al$_2$O$_3$ in shell was changed from about 6 nm to 200 nm and the thickness of Al$_2$O$_3$ shell was changed from about 400 nm to 1000 nm by changing the regime for Al/Al2O3 composite production. Experimental results showed that Al$_2$O$_3$ shell was well clutched with aluminum core. Shell structure had cracks aroused by calcination process. Size distribution for obtained composites was very close for that of initial aluminum powder. All of these characteristics recommend the obtained Al/Al$_2$O$_3$ composites for additive manufacturing.

Keywords: Al/Al$_2$O$_3$ composite, reinforcement, core shell, additive manufacturing, hydrothermal oxidation

1. Introduction
Aluminum has been widely used in automotive, aerospace, and defense industries due to its light weight, high specific strength and excellent corrosion resistance. At the same time, compared to pure aluminum and various unreinforced aluminium alloys, aluminum-based metal matrix composites provide better mechanical and physical properties, including greater strength, improved high temperature properties, wear resistance and a controlled thermal expansion coefficient [1-3]. One of the most commonly used reinforcements for aluminium and its alloys is Al$_2$O$_3$ [3-5]. Commonly, it improves the compressive strength and the wear resistance of produced material. Mechanical properties of Al/Al$_2$O$_3$ composites recommend this type of material for auto components that are working at high temperatures (200–300 °C) or in aggressive atmospheres (except water) [6]. Such composites can be used for example in such automobile parts as engine piston, cylinder liner and brake disc/drum [7].

Although, Al/Al$_2$O$_3$ composites possesses useful advantages, their application has been limited compared to its potential because of their high processing costs and the lack of a feasible fabrication method. Usually they are produced by liquid phase or solid phase (mechanical) milling. Milling process is usually based on the mixing of the two components (Al and Al$_2$O$_3$) of the composite. One of the main aims in this field is the obtaining of uniform distribution of the Al$_2$O$_3$ particles in the Al matrix.

On the other hand, in recent years the additive manufacturing has attracted widespread attention for its ability to produce high quality structural metallic components with greatly reduced cost and improved lead-time. Additive manufacturing for metals usually uses metal laser sintering technology
that creates parts in a layer-by-layer fashion by selectively fusing and consolidating thin layers of powders with a scanning laser beam. This technology allows producing parts with high accuracy and detail resolution, good surface quality and excellent mechanical properties.

One of the most important constructive materials is aluminum or its alloys that are currently produced by laser sintering, in particular with compositions suitable for casting [8]. Initial raw represents usually the powder with specific composition. As a powder based process, this additive manufacturing provides also great opportunity to consolidate second material, particularly Al₂O₃, with aluminum to form novel metal matrix composites. In this case the issue of uniform distribution of Al₂O₃ additive in Al volume must be also decided in order to produce high-quality product.

It is evident that core shell Al/Al₂O₃ composite with straight clutch of the components is very promising material for additive manufacturing. Coating process is attracting more and more attention in the preparation of composite materials as it improves the dispersion of the powders, controls the interfacial properties and introduces a uniform incorporation of minor additives for better microstructure control and desired functional properties [9]. Aluminum oxide shell on aluminum surface not only stabilize aluminum dispersion but also make it possible to control inter-particle interaction.

Core shell Al/Al₂O₃ structure can be achieved by aluminium oxidation. Oxidation medium represents usually air (oxygen) or water. During aluminium oxidation the shell of aluminium oxide or hydroxide that is produced makes an obstacle for oxidizer to penetrate to the metallic core and so slows or even stops further oxidation. There are some attempts to provide high oxidation degree of aluminum. High oxidation degree of aluminum in Al/Al₂O₃ composite was attained by air passivation of ultrafine Al particles prepared by plasma evaporation method [10]. Microwave assisted oxidation of aluminium micron powder in air was proposed to obtain Al/Al₂O₃ composite with relatively high Al₂O₃ thickness in [11]. However, above mentioned methods require high energy input to produce Al/Al₂O₃ composites.

High degree of aluminum oxidation can be achieved by aluminium oxidation in water. In our previous work we proposed a method for preparation of Al/Al₂O₃ composites by hydrothermal oxidation of aluminum at 280-350 °C and subsequent thermal treatment in muffle furnace to convert aluminum hydroxide to γ-Al₂O₃ [12]. That was realized on recently created plant based on continuous reactor for hydrothermal oxidation of aluminium [13]. It was shown that oxidation degree for aluminum powder with average size of 22 μm is changed from 40 to almost 100 % when temperature in hydrothermal reactor changed from 280 to 350 °C.

To simplify the process of Al/Al₂O₃ composites production through aluminium oxidation in water in present study we concentrated on aluminium oxidation in batch type reactor in temperature range of 100-200 °C. Oxidation process at these temperatures can be realized at considerably lower pressures (up to 2 MPa) than at temperatures of about 300 °C when pressures of 10 MPa and higher are needed in order to maintain the water in liquid state. The aim of present work is the synthesis of Al/Al₂O₃ composites through aluminum oxidation in water at 100-200 °C with controllable oxidation degree of aluminum and so the depth of Al₂O₃ shell propagation in composite’s matrix. Investigation of structural properties of Al/Al₂O₃ obtained is one of the main tasks of present work.

2. Materials and methods

Aluminum powder used in experiments was purchased from Rusal. Powder represents spherical particles with average size of about 40 μm.

The Al/Al₂O₃ composites were produced in three main stages: oxidation in autoclave, drying in oven, and calcination in muffle furnace. Al/Al₂O₃ composites were prepared in five different regimes. Parameters of these regimes are shown in table 1. In regime A the suspension consisting 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 than such “wet” aluminum powder was dried. In regime A 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 was applied, corresponding parameters are shown in table 1. In all experiments the temperature of drying and temperature of calcinations were the same and equaled to 120 and 600 °C respectively.

**Table 1.** Parameters of experiments in which the Al/Al₂O₃ composites were prepared.

| Regime | Suspension composition | Autoclave oxidation stage parameters | 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 | Maximum heating temperature, ºC = - | Maximum pressure, bar = - | - | 120 | 600 |
| B      | 1 kg of aluminum and 3 kg of water 1.5 kg of aluminum and 2.8 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 |

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

Aluminum oxidation degree evaluation was carried out in experimental plant described in [13-14]. That experimental plant is based on glass reactor with stirring and gas flow meter. The samples are loaded into 1 M KOH aqueous solution at 90 °C and the yield of hydrogen was precisely measured in order to calculate the degree of aluminum oxidation. Aluminum oxidation degree was uniquely defined from the yield of hydrogen. The error in aluminum oxidation degree evaluation was no more than 1 %.

Surface morphology of solid products was studied (Figure 1) on JEOL JSM-7401F scanning electron microscope (SEM).

![SEM images of initial aluminum powder.](image-url)
Powder size was measured with the help of laser diffractometer Fritsch Analysette 22. Phase composition of oxidation product was studied by X-ray diffraction using DRON-2 (USSR). Solid oxidation products were dried at 120 °C using Binder VD-53 vacuum oven. For calcination at 600 °C a muffle furnace LHT 08/16 (Nabertherm) was used.

3. Results and discussion
In all conducted experiments aluminum oxidation in water starts at about 68 °C. It was registered by hydrogen evolution that started at about 68 °C in each regime. It can be explained by partial permeability of an oxide layer and decreasing of water viscosity with temperature increasing that promotes the penetration of water to the metal.

Autoclave’s temperature and pressure as well as the yield of hydrogen during experiments in regimes B-E. It is seen that the increasing of autoclave temperature lead to the increasing of volume of hydrogen formed in the autoclave and passed through the gas drum counter. It should be noted that this volume of hydrogen can not be used for aluminum oxidation degree evaluation because of several reasons. At first, in the end of experiment (before the cooling of the autoclave) some unknown amount of hydrogen remained in the autoclave and other vessels, and at second, aluminum continues oxidation during the drying and calcination processes. Thus, the evaluation of aluminum oxidation degree in Al/Al2O3 composites was carried out after the drying and calcination.

Table 2 shows the results of aluminum oxidation degree evaluation for experiments in regimes A-E. Values of oxidation degree were determined experimentally by dissolution of produced samples in hot alkali aqueous solution. Oxidation degree value shows the part of initial aluminium that was oxidized and transformed into Al2O3 (after oxidation and calcination). 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 short-term regime B gives 10.9 % oxidation degree. Further increasing of autoclave’s maximum temperature and duration (reaction time) of oxidation process leads to the increasing of oxidation degree. Regime E with maximum temperature of 200 °C and oxidation duration of about 2 h results in oxidation degree of 21.3 %.

Table 2 shows also the content of Al and Al2O3 in obtained composites.

### Table 2. Aluminum oxidation degree, and the contents of Al and Al2O3 for Al/ Al2O3 samples obtained in experiments in regimes A-E.

| Regime | A  | B  | C  | D  | E  |
|--------|----|----|----|----|----|
| Oxidation degree (% X) | 5.5 | 10.9 | 14.5 | 17.4 | 21.3 |
| Content of Al (C$_{Al}$), wt.% | 90.1 | 81.2 | 75.7 | 71.5 | 66.2 |
| Content of Al2O3 (C$_{Al2O3}$), wt.% | 9.9 | 18.8 | 24.3 | 28.5 | 33.8 |

These values are calculated from aluminium oxidation degree values. The content of aluminum (wt.%) in Al/Al2O3 composite can be determined by the following equation:

$$C_{Al} = \frac{100 - \frac{X}{100 + 0.89 \times X}}{100} \times 100,$$

(1)

where X (%) is the degree of aluminium oxidation (%). Equation (1) takes into account that 1.89 kg of Al2O3 is produced from 1 kg of Al (after oxidation and calcination). The content of aluminium oxide (wt.%) in Al/Al2O3 composite is determined by the following equation:
\[ C_{\text{Al}_2\text{O}_3} = 100 - C_{\text{Al}}. \]  

(2)

The increasing of temperature and duration (reaction time) of autoclave’s oxidation leads to the change of microstructure of Al/Al$_2$O$_3$ composites. Figure 2 shows the obtained product. It is seen that the particles did not change their spherical shape after oxidation. SEM images show that aluminum surface was covered with a layer of aluminum oxide and the thickness of oxide layer is about 400 nm.

![SEM images of the product.](image)

Figure 2. SEM images of the product.

From SEM images with higher resolution it can be seen that the resulting oxide layer has an irregular "petal" structure formed from alumina crystals with the size of about 6 nm. In contrast to the sample obtained in regime A (with a degree of oxidation of 5.5%) in a sample obtained in regime B (with a degree of oxidation of 10.9%), relatively large crystals were also observed on the surface of the particles in addition to the relatively small "petals". This can be explained by the local dissolution of the "petals" and by the crystallization of the hydroxide on the relatively large crystals that work as nuclei. It can be noted that an increase in the degree of oxidation of the aluminum is accompanied with the coarsening of the alumina crystals. Reaction temperature and duration increasing lead to the enlargement of Al$_2$O$_3$ crystals due to the growth of aluminium hydroxide crystals during autoclave oxidation.

From SEM images it is seen that Al$_2$O$_3$ shell is well clutched with aluminum core. The use of such powder as raw in additive manufacturing must decide the issue of uniform distribution of Al$_2$O$_3$ in Al-based matrix. It was experimentally established that the amount of aluminum oxide that has broken off from the surface of the spherical particles increases with increasing of the duration of oxidation process. Such Al$_2$O$_3$ particles can be seen in SEM images; these particles are detached from the
surface and presented in the product as individual fine alumina particles. But amount of such $\text{Al}_2\text{O}_3$ particles in obtained Al/$\text{Al}_2\text{O}_3$ composites as it can be seen from SEM images is negligibly small.

![Figure 3. Microstructure transformation due to calcination of oxidation product (cracks appearance).](image)

![Figure 4. Size distributions for initial aluminum powder (1) and Al/Al$_2$O$_3$ composites with aluminum content of 90.1 (2) and 66.2% (3).](image)

The size distribution for initial aluminum powder and Al/$\text{Al}_2\text{O}_3$ composites with 90.1 (regime A) and 66.2% (regime E) aluminum content. It is seen that size distribution for composites is very close for that of initial aluminum powder. Core shell composites have some more prolonged distribution that can be explained by particles adherence during thermal treatment of oxidized products. But in general, such close size distribution allows supposing that aluminum can be easily replaced by obtained Al/$\text{Al}_2\text{O}_3$ composites in additive manufacturing plant without any change of its dosage system.

X-ray analysis indicated that in the products obtained in all the regimes only two crystalline phases, aluminum and $\gamma$-$\text{Al}_2\text{O}_3$, are presented. These results agree with thermal decomposition sequence of aluminum hydroxides 22. Calcination at 600 °C is applied to transform all forms of aluminum
hydroxide into unhydrous aluminum oxide. It is important to note that the content of chemically and physically adsorbed water must be minimized in Al/Al₂O₃ before laser sintering process because it can cause unnecessary steam and hydrogen generation inside additive manufacturing plant.

4. Conclusion
Presented work described simple and potentially energy efficient way for synthesis of Al/Al₂O₃ composites that can be used in additive manufacturing. Synthesis method is based on aluminum powder oxidation in water in temperature range of 100-200 °C. Drying and calcination at 600 °C were applied to transform all forms of aluminum hydroxides to aluminum oxide.

It was shown the possibility to control the aluminum oxidation degree (content of aluminium) in produced Al/Al₂O₃ composites. Aluminum oxidation degree and the content of aluminum in obtained Al/Al₂O₃ were changed from 5.5 % and 90.1 % to 21.3 % and 66.2 % respectively by changing the temperature (pressure) and duration of the process of aluminium oxidation in autoclave. It was shown that with autoclave’s temperature increasing the size of single crystals of Al₂O₃ shell is increased. It is increased from 6 nm to 200 nm by autoclave’s temperature increasing from 100 to 200 °C. The thickness of Al₂O₃ shell is also increased from about 400 nm to 1000 nm by autoclave’s temperature increasing from 100 to 200 °C.

Results showed that Al₂O₃ shell is well clutched with aluminum core. Shell structure has cracks aroused by calcination process. Size distribution for obtained composites is very close for that of initial aluminum powder that is currently used in additive manufacturing. All of these characteristics recommend the obtained Al/Al₂O₃ composites for additive manufacturing with laser sintering.

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