Partial oxidation of aluminum powder for obtaining a controlled amount of aluminum oxide on the surface of aluminum

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Abstract. This work is devoted to the study of the process of partial oxidation of aluminum powder with hydrogen generation and the production of a metal-ceramic product that can be used in the production of various manufacturers such as additive manufacturing (AM) engineering technologies, machine building and so on. The released hydrogen can be effectively used in the form of an energy carrier that will contribute to reducing the cost of production and reduce the cost of the final product.

1. Introduction

In the world, additive manufacturing (AM) for the production of metal parts [1-5] is developing rapidly and will be a priority technology for the aviation industry, the space industry, and machine building. The processing parameters, such as laser power, scanning speed and powder feed rate determine the characteristics of AM components.

Technologies of growing metal parts have opened the possibility of producing new structural metal composites based on aluminum [6-7]. However, there are difficulties in using AM based on metals and their introduction into production. These include the quality of initial metal and parts, residual stresses, internal porosity.

The alloy containing aluminum is ideal for selective laser melting to manufacture complex components with high strength requirements. At present, a number of metal composite materials on aluminum matrixes reinforced with aluminum oxide have been developed. There is a problem of aluminum oxide just proportion in the metal, its wettability and technological yield of Al\textsubscript{2}O\textsubscript{3}. Aluminum powders with a grain size distribution of 20 to 120 \textmu m for additive printing are used. The porosity is formed due to the powder size in the wide range. If using spherical aluminum particles with a small size range, it can obtain high quality parts by AM. This facilitates a more compact placement of particles in a certain volume and a good "flow" of the powder composition in the feed systems with a minimum resistance. The amount of aluminum powder, the ratio of Al/Al\textsubscript{2}O\textsubscript{3} is important by growing metal parts.
The studying the process of aluminum oxidation in different ways and obtaining an aluminum oxide of 10 to 30 % is an important goal. Given the idea of certain content of aluminum oxide, these results suggest that there may be broader viability for additively manufactured parts. The studies of the change dynamics of the spherical aluminum particles are presented. For the analysis of the obtained samples, transmission electron microscopy and X-ray phase analysis were used [8-14].

2. Experimental

2.1. Description of the installation

The key step in the process of obtaining a partially oxidized aluminum powder is the autoclave oxidation of the aluminum powder. The properties of the product obtained depend on the oxidation parameters (reagents ratio, temperature, interaction time).

The scheme of the autoclave is shown in Fig. 1. Inside the reactor (2), the reaction medium is stirred by an anchor 2-blade agitator. The speed of rotation of the stirrer is about 100 rpm. The mixer is made of SS316 steel with Teflon coating. The following devices are provided on the reactor cover: a manometer (M); gas outlet connector; water injection valve (V2) and a ball valve for injection of a suspension (V1), a resistance thermometer (T).

Heating of the reactor-autoclave is controlled by the control panel (controller). During the operation of the autoclave, the pressure, temperature and speed of rotation of the mixer are measured. Depending on the readings of pressure and temperature sensors, water is supplied to the reactor or the speed of rotation of the mixer is changed. The system of separation of water vapor is designed to condense water vapor from a mixture of steam and hydrogen leaving the reactor, return condensed water and supply hydrogen to the consumer (hydrogen-utilizing device).

The reactor vessel has a volume of 5000 ml. The vessel is vertical, cylindrical, made without welding and other connections made of SS316 stainless steel. All parts in contact with the reaction medium are made from SS316. The reactor is heated from an electric ceramic belt heater with thermal insulation and a temperature controller. The drive of the mixing device is an electric motor with alternating current with a frequency converter and a digital speed display. Engine power of 0.18 kW. The sealing of the stirrer shaft is carried out using magnetic coupling. Magnetic seal - with zero leakage (declared by the manufacturer), maintenance-free. The maximum torque is 40 kg*cm (3.92 N*m).
A mixture of steam and hydrogen comes from the autoclave reactor to the heat exchanger (5), where the water condenses and flows back into the reactor. A pressure sensor (M) is installed on the line between the heat exchanger and the pressure regulator, which measures the pressure to the regulator corresponding to the pressure inside the reactor. The heat of steam condensation leaving together with hydrogen from the reactor is transferred to the water of the second circuit. The pressure regulator (V6) maintains a certain pressure in the reactor (pressure "to itself"). After the pressure regulator hydrogen with the remaining water enters the bubbler (3), where a final separation of liquid and gaseous phases is carried out. From the bubbler hydrogen is directed to the gas drum counter (4).

2.2. *Properties of the initial aluminium powder*

The distribution of aluminum particles in size is shown in Fig.2. The average diameter of the particles is 40 microns.
The initial aluminum powder contains 770 μg/g of iron (0.077%). Also, based on the obtained elemental composition (analysis of the sample of aluminum was determined by mass spectrometry with inductively coupled plasma using a mass spectrometer with inductively coupled plasma ThermoScientific X-2), it follows that the total aluminum content in the powder was 99.89%.

A micrograph of the powder obtained with the JEOL JSM-7407F scanning electron microscope is shown in Fig.3. The image show that the initial aluminum powder consists of agglomerates. The size of the structural units of these agglomerates is in 1-10 microns. The particles have a relatively smooth surface, on which there are various defects (Fig.3).

2.3. Description of the process of obtaining partially oxidized aluminum powder
The production of partially oxidized aluminum powder takes place according to the scheme shown in Fig.4.
As can be seen from the scheme, the process of obtaining partially oxidized aluminum powder consists of three main stages: oxidation, drying and heat treatment.

Before the oxidation stage the weighing of initial aluminum powder and water is preceded. The mass ratio of water to aluminum in the suspension is selected depending on the required degree of oxidation. The distilled water was used. The prepared suspension is poured into the autoclave through the ball valve. Further, the ball valve closes. The reactor heating and stirring of the reaction space are activated. The reactor is heated by an electric heater at a given speed to a certain temperature. Throughout the experiment, the readings of pressure and temperature sensors inside the reactor, as well as the volume of hydrogen released, are monitored.

If the temperature inside the reactor exceeds a certain level, water from the distilled water storage tank (6) is added to the reactor. During the oxidation process, the hydrogen formed together with the water vapor generated inside the reactor by the thermal energy of the exothermic aluminum oxidation reaction enters the heat exchanger. In the heat exchanger, the water condenses and returns back to the reactor. When the pressure inside the reactor reaches a certain value, the pressure regulator is activated, and hydrogen from the heat exchanger enters the bubbler. Solid reaction products are removed with water from the bottom of the reactor through a shut-off valve (8) into the tank receiving the oxidation product. For more complete removal of reaction products from the reactor and its washing and cooling, additional water is supplied to the reactor from the distilled water storage tank. After that, stirring is switched off.

The resulting oxidation of the slurry is partially oxidized aluminum powder is divided into stages of deposition. As a result of sedimentation is the deposition of aluminum particles on the bottom of the tank. The phase separation takes place by decantation.

The next technological stage is drying of the oxidized aluminum powder obtained in the autoclave. To do this, the wet aluminum powder is poured into pre-suspended stainless steel tanks, weighed and placed in the Binder VD drying oven at a temperature of 120 °C.

The final stage of the process of obtaining partially oxidized aluminum powder is heat treatment. Heating of the product was carried out in the muffle furnace Nabertherm LHT 08/16 at a temperature of 600°C for 5 hours.

The result is a product that is an aluminum core coated with a porous layer of $\gamma$-Al$_2$O$_3$.

Two products with different oxidation degree were produced in this work. Those products were produced in different regimes. In the first regime, the oxidation of aluminum powder was carried out when at a temperature in the autoclave did not exceed 120 °C, the holding time in the reactor – 60 minutes. In the second regime, the temperature of aluminum powder in the autoclave did not exceed 180 °C, the holding time in the reactor – 120 minutes. In first experiment the reactor was loaded by 900 g of aluminum and after 60 minutes 80 liters of hydrogen were produced. In second experiment the reactor was loaded by 1500 g of aluminum and after 120 minutes 300 liters of hydrogen were produced.

3. Results and discussion

3.1. Particle size distribution

Fig.5 shows the particle size distribution of partially oxidized aluminum. The particle diameter is in the range of 2 – 200 μm. The average diameter of the particles is 41 microns, which corresponds to the average size of the particles in the initial aluminum powder.
Figure 5. The histogram of distribution of particle size for the partially oxidized sample.

3.2. Microscopy and the generation of hydrogen in experiments

Fig.6a, 6b shows the product obtained in experiment with the oxidation of aluminum powder at a temperature of 120 °C, the holding time in the reactor of 60 minutes, and hydrogen yield of 80 liters.

Figure 6a. Image obtained by scanning electron microscopy in the approximation of 2 microns for a sample with a hydrogen output of 80 liters.

The images show that the relatively smooth surface of the aluminum powder was coated with a layer of aluminum oxide with a thickness of up to 500 nm (Fig.6a, 6b).

The image for product of aluminum powder oxidation at a temperature of 180 °C, the holding time in the reactor of 120 minutes, and hydrogen yield of 300 liters, is shown in Fig.7. It shows that the oxidation product is covered by oxide film with the thickness of approximately 1 micron.
3.3. The results of x-ray analysis

The main objective of the x-ray analysis is to identify the different phases in their mixture based on the analysis of the diffraction pattern formed by the sample under study. Determination of the substance in the mixture is carried out by a set of its interplane distances and relative intensities of the corresponding lines on the radiograph. The x-ray phase analysis was carried out on the x-ray diffractometer DRON-2 (made in USSR). As a result of the analysis of the obtained patterns, it was found that, in addition to metal aluminum, traces of the presence of fine γ-Al₂O₃ were registered in the sample. The rest of the material is in amorphous (or x-ray amorphous) state.

Figure 6b. Image obtained by scanning electron microscopy in the approximation of 4 microns for a sample with a hydrogen output of 80 liters.

Figure 7. Image obtained by scanning electron microscopy in the approximation of 4 microns for a sample with a hydrogen output of 300 liters.
4. Conclusion
Two samples of partially oxidized aluminum powder were produced in reactor-autoclave in distilled water. The first sample was oxidized with hydrogen output of 80 liters obtained from oxidation of 900 g of aluminum and the second sample was oxidized with hydrogen output of 300 liters obtained from oxidation of 1500 g of aluminum. According to the microscopic analysis it was shown that the products keep the spherical shape, and the thin layer of aluminium oxide (after heat treatment at 600 °C) is formed on the surface of aluminium. According to the results of x-ray analysis it was shown that products contain two crystallic forms: aluminum and $\text{Al}_2\text{O}_3$ that is predominantly in amorphous state.

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