ADSORPTION CAPACITY OF WATER-OXIDIZED LANTHANUM-DOPED ALUMINUM ALLOY POWDER

A. Ryabina, V. Shevchenko, D. Eselevich

Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia

anna-ryabina@yandex.ru

The adsorption of nitrogen onto the surface of lanthanum-doped ultrafine aluminum (UFA) powder was studied before and after aqueous oxidation under relative adsorbate (Pa/Po) pressures from 0 to 1 using low-temperature nitrogen adsorption method in a volumetric static vacuum facility. The adsorption isotherms are considered for their compliance with the isotherms in the classification of S. Brunauer, L. Deming, U. Deming and E. Teller. The obtained results confirm that treatment of REM-containing powders with water leads already at room temperature to the formation of new phases and affects their morphology. It is shown that a large role in the properties of water-treated powders belongs to the nanopores formed between crystallites on the surface of particles in the process of oxidation with water and during subsequent thermal dehydration. The adsorption properties of Al – 3% La sample were examined by the following methods: analysis of adsorption-desorption isotherms of vapors (statistical volumetric method) based on nitrogen adsorption at 78 K, electron microscopic technique, and X-ray analysis. The specific surface area and porosity of the powders were calculated.

Keywords: adsorption, ultrafine powders, pores, specific surface area.

1. Introduction

Hydrothermal synthesis is an effective method for producing porous aluminum hydroxides used as adsorbents, catalysts and catalytic materials carriers [1,2]. Comprehensive information about the interaction of aluminum powders of different dispersion with water is presented in Ref. [2]. In this study, we show that the interaction is suppressed by high protective properties of the oxide film on the surface of particles. One of the promising methods for destruction of the barrier layer is alloying of aluminum with active metals. So, the interaction of aluminum-gallium and thallium-tin alloys with water was examined in Refs. [3–7]. The distribution of alloying elements on the grain boundaries leads to active intergranular corrosion and to destruction of metal to an ultrafine and nanosized state, complete transformation into aluminum hydroxide taking place for a shorter period of time than for pure aluminum. Later it was found that the presence of gallium can be used to advantage for the production of hydrogen [8]. At the same time, the use of alloy powders makes it possible to affect the physicochemical and mechanical properties of materials synthesized by hydrothermal synthesis, as well as their adsorption capacity.

This paper deals with the adsorption capacity of aluminum lanthanum alloy powders and the products of interaction with water obtained at room temperature.

2. Methods, results and discussion

The alloy synthesis, powder production and experiment procedures were the same as described previously [9,10].

The objects of this study were prepared by spraying the melts with nitrogen followed by recondensation of gas plasma under low-temperature plasma conditions on GNIICHTEOS plants [11].

Before and after the experiment, the samples were weighed on a Shimadzu AUW 120D high-accuracy electronic balance.

The content of active aluminum powders during hydrotreatment was determined by the volumetric method – from the volume of evolved hydrogen. The adsorption properties were studied on a Sorptomatic plant from nitrogen adsorption on the particle surface. The specific surface area and porosity were calculated by the BET and Barrett, Joyner and Halenda (BJH) methods [12].

Surface oxidation of aluminum powder with water leads to a dramatic increase in the specific surface area. UFA can be classified with non-porous materials. Its specific surface area was 7 m^2/g before and 30 m^2/g after hydrotreatment. UFA powder was stored in a conditionally sealed package and interacted with atmospheric moisture during storage, therefore it already contained oxide phases because the active aluminum content was $\sim 80\%$. The electron micrographs of the UFA sample before and after water treatment are presented in Fig. 1. The UFA powder particles before aqueous oxidation had a spherical form of about 5–10 microns in diameter, which were coated with smaller particles formed when the initial ASD–4 type alloy powder passed through a plasmatron. After interaction with water, the particles were bound agglomerates differing greatly in size. As is seen, they were the same spherical particles coated with a fine fraction of aluminum oxide hydroxide AlOOH. Analysis of the phase composition of the samples after water oxidation was carried out on a Shimadzu diffractometer (Cukα radiation) using the JCPDS standard database. The content of active aluminum decreased by 14%.

The Al – 3% La powder before interaction with water was a non-porous sample corresponding to the isotherm of type 2. After water treatment, the Al – 3% La sample belongs to mesoporous materials and corresponds to the isotherm of type 4, according to the recommendations of the International Union of Pure and Applied Chemistry (IUPAC) [12].

The adsorption isotherm of Al – 3% La has a hysteresis loop, Fig. 2. According to the IUPAC classification, hysteresis for Al – 3% La is of H3 type, i.e. this material has near-slit-like pores. The isotherm of Al – 3% La after water oxidation is typical of porous aggregates with a developed network of intersecting pores [13].

The structure of porous carriers is generally characterized not only by the specific surface area, but also by the pore volume and pore size distribution [12,14].

The porous structure of Al – 3% La sample obtained in the aqueous process was calculated using the Barrett, Joyner and Halenda theory (BJH method) [12,15]. It was found to be of polydisperse nature with mesopores with a narrow size distribution of in the range from 30 to 40 Å, Fig. 3. The total pore surface area was 45 m^2/g. The total pore volume was 0.058 cm^3/g. The specific surface area of the sample before and after interaction with water was respectively 20 and 60 m^2/g.

Although lanthanum is not registered in any form by XRD, the presence of lanthanum had an influence not only on the reaction between aluminum and liquid water stimulating oxide hydroxide formation, but also on the structural characteristics of the synthesized product
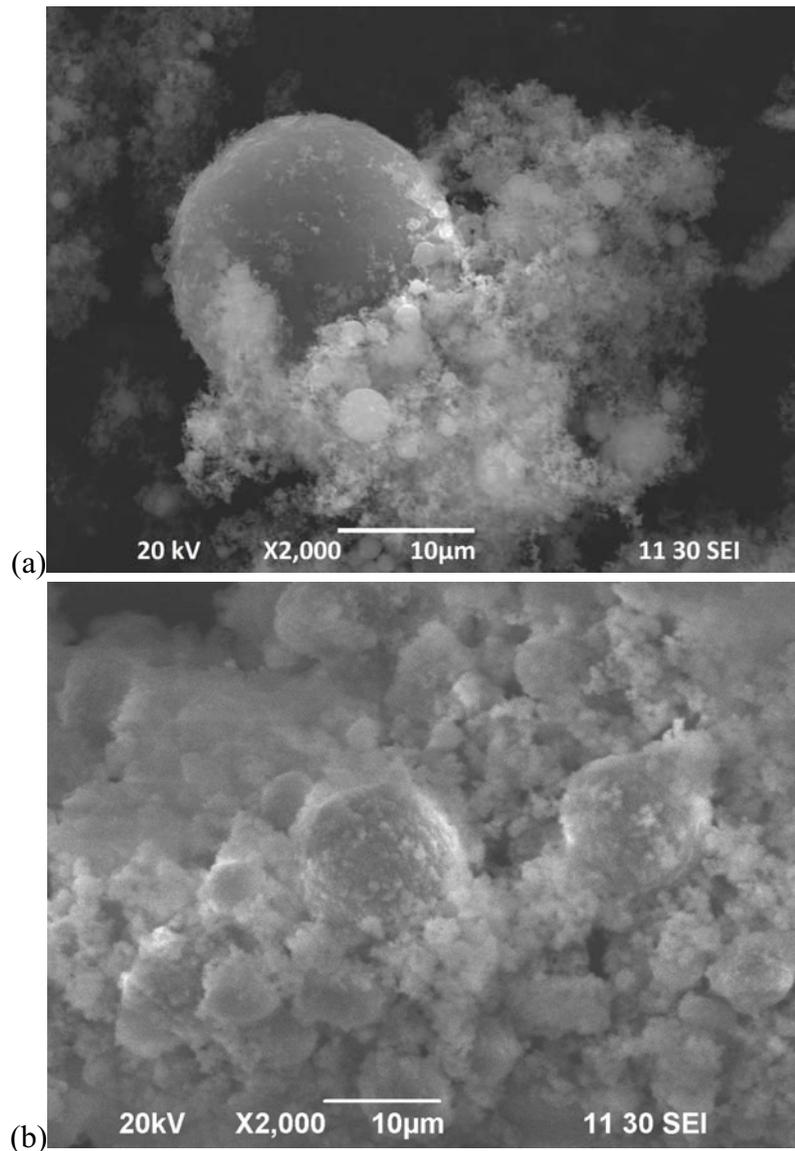
FIG. 1. Micrographs of alloy powders: (a) initial UFA, (b) UFA after interaction with water (48 h)

increasing the degree of its amorphism. The amorphism of Al – 3% La powder after hydrotreating is also attested to by the presence of a wide band (halo) inherent in the amorphous phase corresponding to boehmite AlOOH, Fig. 4.

According to electron microscopic examination of the Al – 3% La sample after water oxidation, the powder has a loose structure (loose agglomerates of amorphous particles) where plates with slit-like pores are observed, Fig. 5. Thus, the pseudoboehmite precipitate produced at a temperature not higher than 30 °C consists of fine crystal grains forming the porous structure of slit-like pores with the average pore diameter of 3–4 nm that are combined into secondary particles (flakes) containing a large amount of colloidal-bound water. This water is held by the hydrate very firmly and can be removed only by drying at 110–130 °C. The entire sample reacted with water completely, as evidenced by phase and volumetric analysis. The specific surface area increased up to 60 m^2/g.
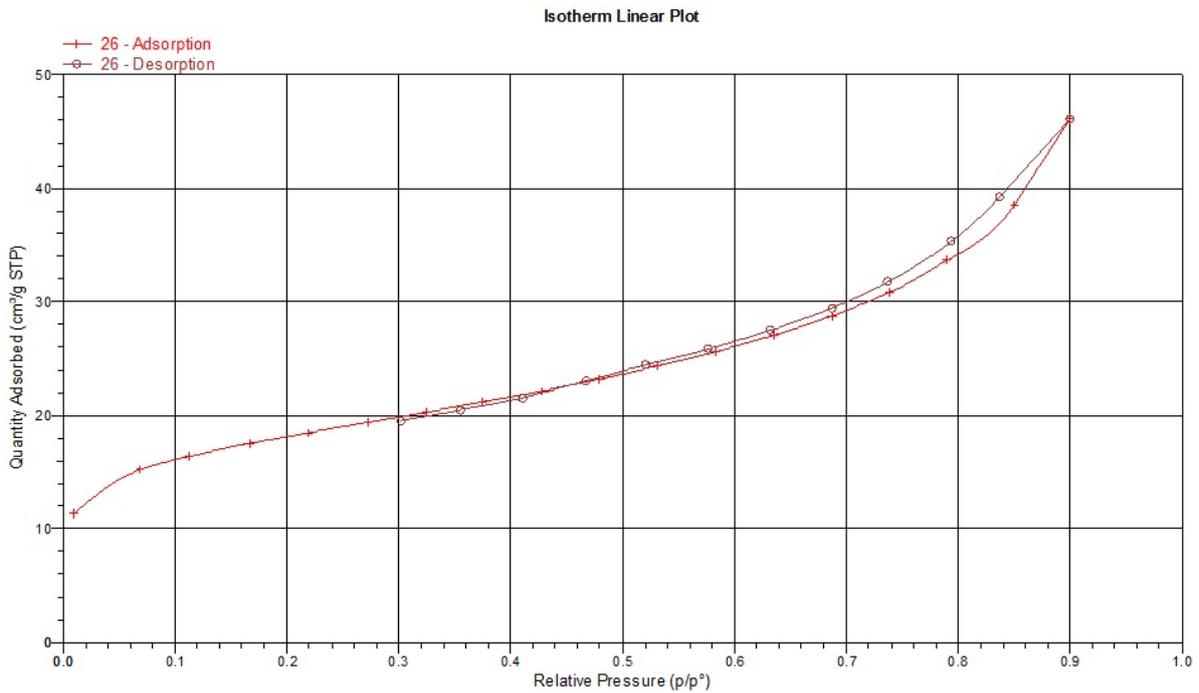
FIG. 2. Nitrogen adsorption isotherm on the surface of Al – 3% La powder after interaction with water
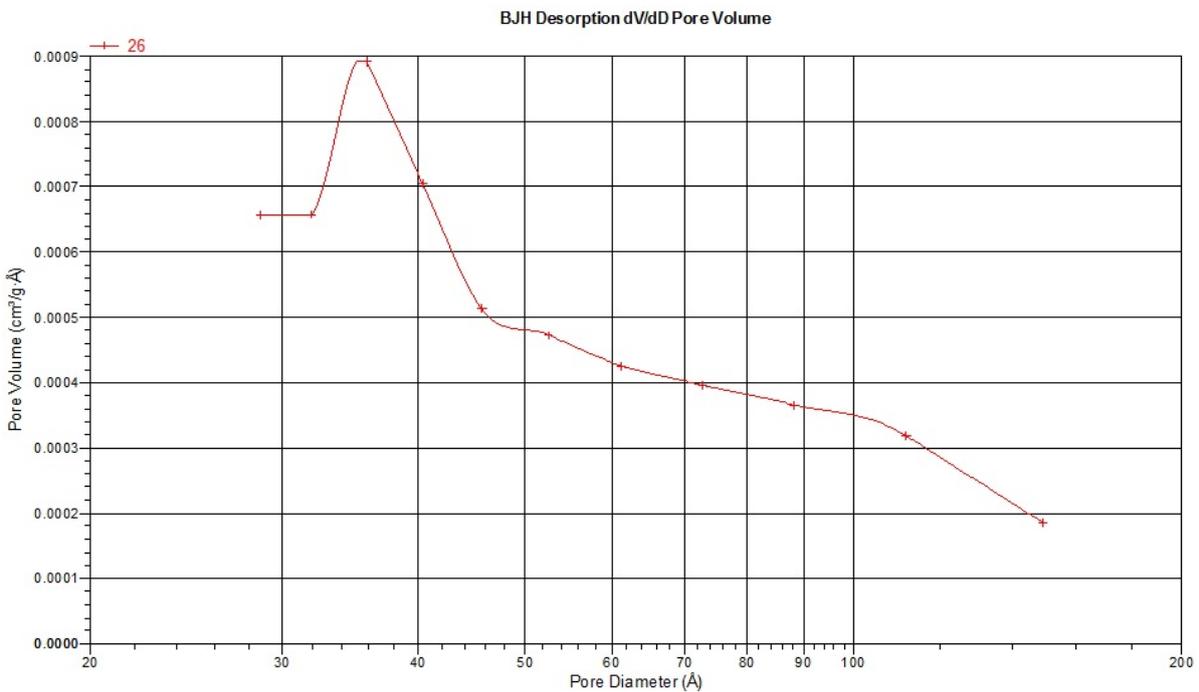
FIG. 3. The pore diameter distribution curve for the Al – 3% La composition

The results obtained showed that at room temperature the process of interaction of Al – 3% La with water is most likely to flow the scheme: amorphous phase – pseudo-boehmite (AlOON) – boehmite (γ–AlOOH) – bayerite Al(OH)$_3$ – gibbsite Al(OH)$_3$ [16].
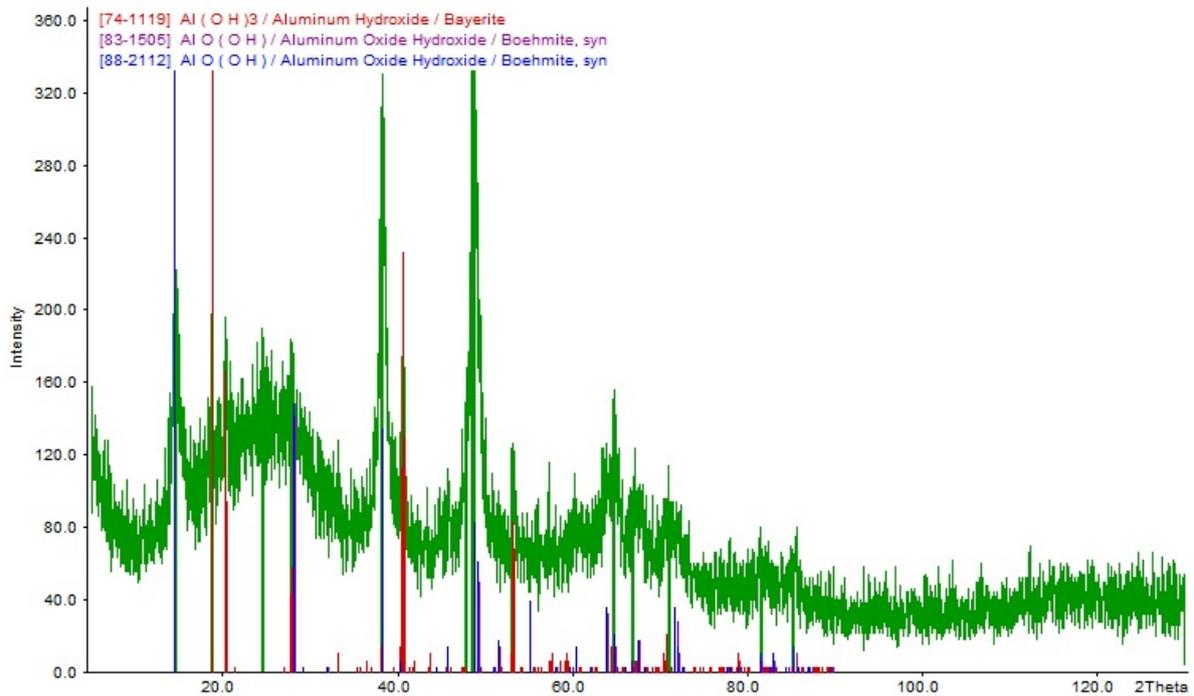
FIG. 4. The diffractogram of water-treated Al – 3% La powder
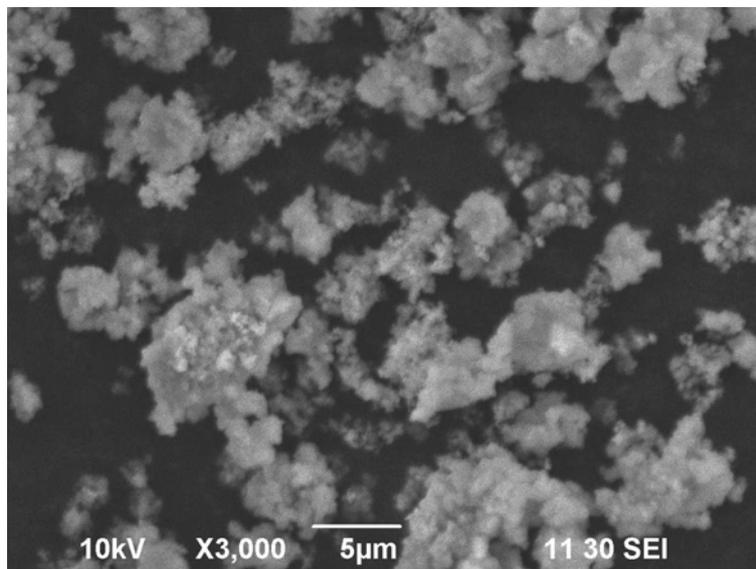
FIG. 5. Microphotograph of Al – 3% La alloy powder after interaction with water (48 h)

3. Conclusions

The interaction of Al – 3% La alloy powder with water at room temperature has been studied for the first time. During 48 h the sample completely reacted with water to form AlOOH and $Al(OH)_3$.

Alloying aluminum with lanthanum activates the interaction process and leads to the formation of nanoscale products with a specific surface area of 60 m^2/g and a narrow size distribution for mesopores, ranging from 30 to 40 Å.

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