Investigation of the surface morphology of ASD-4 powder, modified by V_2O_5

V.G. Shevchenko[1], D.A. Eselevich[2], N.A. Popov[3], D.K. Kuznetsov[4], V.Ya. Shur[5]

[1,2,3]Institute of Solid State Chemistry UB RAS, Ekaterinburg, Russia
[4,5]Institute of Natural Sciences and Mathematics UFU, Ekaterinburg, Russia

***Abstract*— *The changes in the surface layer of aluminum particles treated with V2O5 • nH2O hydrogel were studied by ellipsometry and raster electron microscopy methods. It was shown that at 0.8 wt.% content of metallic vanadium in the modified powder, the particle surface layer has a well developed relief, and a high degree of impregnation is achieved. The values of the thickness of this layer measured by different methods were compared, and the obtained deviations were analyzed.*

***Keywords*— *aluminum powder, surface modification, vanadium pentoxide, microscopy, ellipsometry*.**

I. INTRODUCTION

The use of vanadium oxides for improving the combustion of metal powders has been studied for many years [1-4]. Due to vanadium polyvalence, a large amount of oxides and other compounds formed during its oxidation makes this metal a good oxygen carrier to the reaction zone. Being the most demanded material in this field, vanadium oxide (V) in itself is a strong oxidant and has a melting point close to aluminum, which promotes its use as an additive reducing the ignition temperature and increasing the speed and heat of combustion of powder aluminum. In the liquid state, vanadium pentoxide, due to a low surface tension [5], penetrates into the pores and cracks of the oxide film on the surface of aluminum particles [1, 6, 7], promoting active oxidation of aluminum with simultaneous formation of $AlVO_4$. The application of $V_2O_5 \cdot nH_2O$ gel on the surface of aluminum powders of the ASD-4 type [8] significantly increases their specific surface, without changing the shape of the metallic particles, which positively affects their rheological properties [6]. We have established that the aluminum powders modified with $V_2O_5 \cdot nH_2O$, $Na_2V_{12}O_{31} \cdot nH_2O$, $LiV_{12}O_{31} \cdot nH_2O$, $Na_2MoV_{11}O_{31} \cdot nH_2O$ and $6V_2O_5 \cdot B_2O_3 \cdot nH_2O$ had twice as large specific surface area as the initial ASD-4, a high storage stability and, according to thermogravimetric data, a high oxidation efficiency in air [6, 7]. It is known [2, 9, 10] that during dehydration of gels the obtained xerogels have a quasi-two-dimensional (2D) layered structure that is easily intercalated at room temperature by metal ions, molecules of organic solvents, organometallic complexes and other compounds. However, the characteristics of the modified powder surface, the geometric parameters of the oxide and modifying layers, the structure and stability of the modified layer remain unknown. Thus, the main aim of the present work is a more detailed study of the morphology, thickness of the oxide and modifying layers in the initial and modified particles of aluminum powder, as well as the stability of the modified layer during heating to the temperature close to the aluminum melting point.

II. EXPERIMENTAL

Aluminum powder ASD-4 with a specific surface area of 0.4 m^2/g was used in the study. The hydrogel $V_2O_5 \cdot nH_2O$ was synthesized by thermohydrolysis of V_2O_5 by pouring the melt into a heat-resistant beaker with intensively stirred distilled water [6]. To increase the vanadium content, the resulting hydrogel was concentrated by evaporation in a water bath. This allowed the samples with ~0.8 wt. % V content to be obtained by single impregnation of the gel.

The thickness of the oxide films on the surface of initial ASD-4 powder and the powder modified with vanadium pentoxide at room temperature in air was estimated using ellipsometry (ellipsometer LEF-3M, $\lambda = 0.638$ nm, angle of incidence $\varphi = 45°$). For the experiments, the powders were compacted in the form of tablets by pressing under pressure p = 29.4 MPa. The compressed tablets had a flat mirror surface. The surface of aluminum powders was shown with the use of electron microscopy. Using a focused ion beam of gallium, the powder particles were cut in a workstation AURIGA CrossBeam (Carl Zeiss, Germany) in vacuum to obtain a picture of their cross section. The beam current was 16 nA at an accelerating voltage of 30 kV. Delicate surface etching was carried out at an accelerating voltage of 30 kV and an ion beam current of 240 pA. The specific surface of the powders was evaluated by the low-temperature nitrogen desorption method (BET method) using a TriStar 3000 automatic analyzer (Micrometrics, USA).

III. RESULTS AND DISCUSSION

The specific surface area of ASD-4 powder after treatment with $V_2O_5 \cdot nH_2O$ gel increased two-fold and amounted to 0.873 m^2/g. Figure 1 shows the general view of a particle of the modified powder cut by ion beam; the surface of neighboring modified particles is also visible. It can be seen that the relief is highly developed and meshy. This provides an increased specific surface area of the particles, with their sphericity being preserved. The above-mentioned improvement in the flow rate of the powder is due, in our opinion, to the lack of moisture absorption by vanadium pentoxide and to the aggregation of metal powder particles during mixing with the hydrogel.

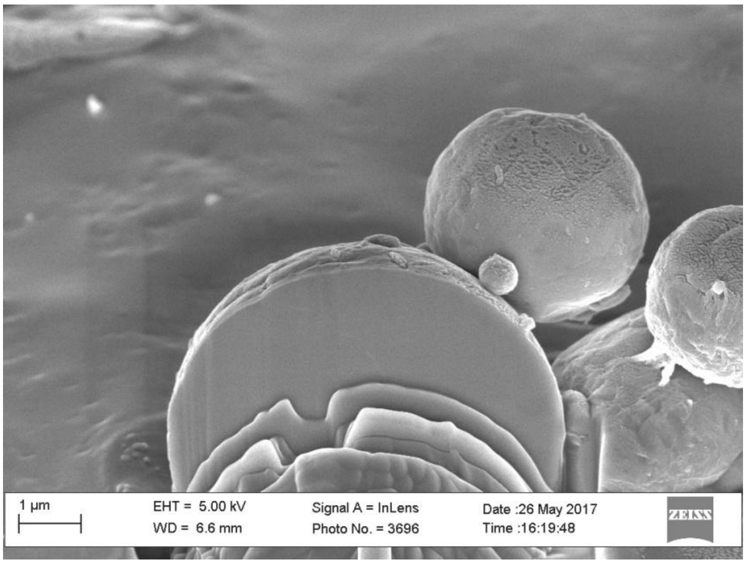

FIG. 1. Electron microscopic images of ASD-4 powder after impregnation with $V_2O_5 \cdot nH_2O$ gel

X-ray phase analysis using synchrotron radiation at the station of channel 4 of the Shared-Use Center “Siberian Synchrotron and Terahertz Radiation Center (SSTRC)” based on VEPP-3 of BINP SB RAS showed that the impregnation of the powder with vanadium pentoxide in the form of a gel does not lead to a variation in the chemical composition of the sample: besides the Al and Al_2O_3 peaks, invariably present on the X-ray patterns of ASD-4, there are weak signals from V_2O_5. The presence of a vanadium pentoxide xerogel in the modified layer is also confirmed by the IR spectra, where the bands at 1010-1005, 770-750 and 510-505 cm^{-1} are observed, which correspond to the frequencies of V-O bond vibrations in the structure of V_2O_5. nH_2O xerogels [6].

Figure 2 shows a cross-sectional view of a particle of the initial ASD-4 powder obtained by a high-resolution electron microscope provided with an ion beam.

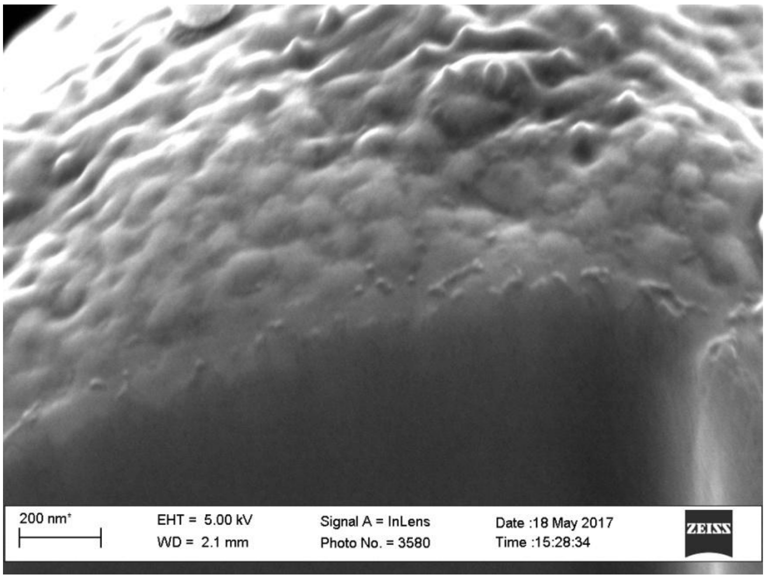

FIG. 2. A cross section of a particle of the initial ASD-4 powder

The upper part of the photomicrograph shows the particle surface relief, the lower part - a smooth ion beam cut deep into the particle interior. A lighter shade of the particle surface is due to the presence of a passivating oxide layer of Al_2O_3. However, due to hardware limitations, it was not possible to clearly distinguish the boundaries between the metal core and the oxide layer and to estimate the oxide layer thickness.

Figure 3 (a, b) displays a cross-section of a particle of modified ASD-4 powder. In this case, the surface film is seen more clearly, its average thickness is about 40 nm. The better contrast is due, first of all, to a larger thickness of the modified layer compared to the passivating film on the original ASD-4. Filming was also carried out in secondary electrons, and a lighter shade of the surface layer means that emission of secondary electrons from the surface layer is higher than from the aluminum core. The secondary electron emission coefficient for dielectric materials is higher than for conductors. An additional contribution to the emission is made by the backward reflected electrons, which, in turn, generate secondary electrons. Since the coefficient of electron reflection increases with increasing atomic number, it is possible in theory to see a varition in the light intensity as a function of the concentration of elements in depth. However, in the presented photographs this gradient is expressed very weakly, and for its detection a greater magnification and point chemical analysis (EDX) are required. The absence of a color intensity gradient in the film depth indicates the incorporation of aluminum and oxygen atoms into the crystal structure of the xerogel during ion etching.

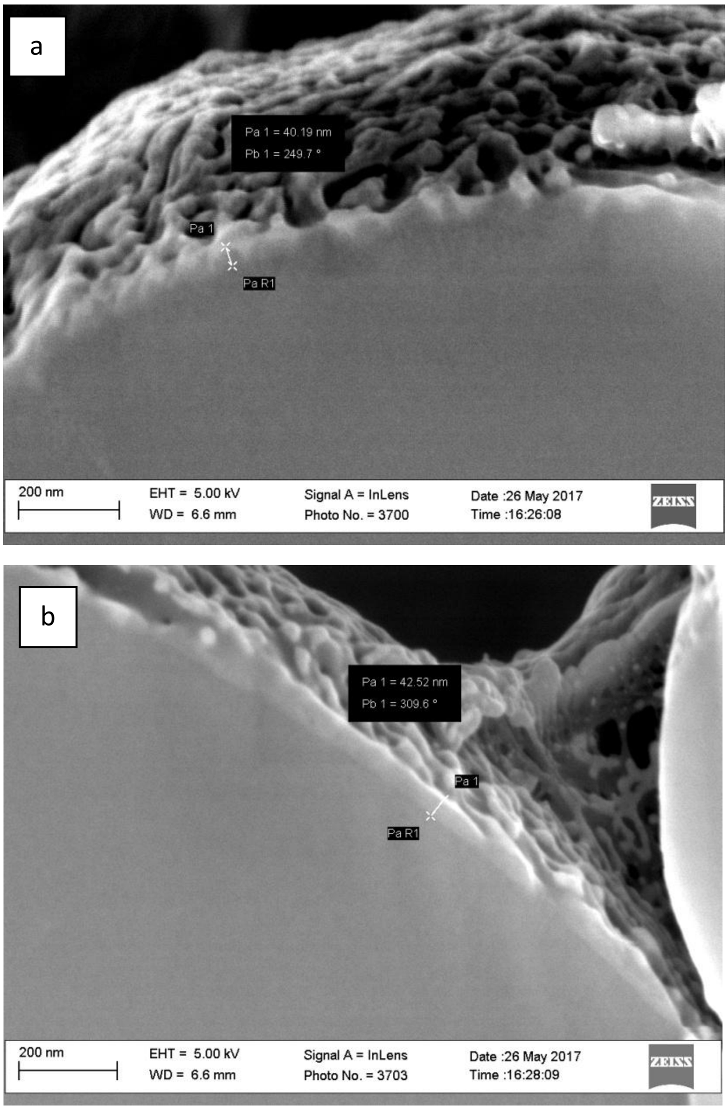

FIG. 3. A cross section of a particle of ASD-4 powder modified by vanadium hydrogel

Figure 3 (a, b) shows that the modified surface has a much more developed net-like relief than the original aluminum powder (Fig. 2). The formation of such a structure can be due to removal of water molecules during xerogel drying and to fixation of the xerogel on the oxide film surface defects. Note also a rather firm adherence of the modified layer to the metallic core, which may also indicate the possibility of intercalation of the xerogel by aluminum ions.

The thickness of the surface layers on the powders was estimated by the ellipsometry method according to the procedure described elsewhere [11]. The object of investigation in this case was the surface of tablets obtained by pressing the investigated powders. The experimental data were processed using a modified nomogram Δ-ψ, intended for the calculation of the thickness (d) and the volume fraction of metal (q) in the powders during their oxidation. The horizontal lines on this nomogram (Fig. 4) correspond to the lines of equal oxide thickness, and the vertical lines – to the corresponding values of q. If the refractive indices of the components of the medium are known - in this case the metal and the oxide (n_{ox} and $N_2=n_{met} - ik_{met}$), then the relationship between them and their volume fractions is expressed by the Maxwell-Garnett equation for the polarizability of molecules [12]:

$$\frac{n^2-1}{n^2+2}=q\frac{n_1^2-1}{n_1^2+2}+(1-q)\frac{N_2^2-1}{N_2^2+2} \tag{1}$$

where q is the volume fraction of metal, (1-q) is the volume fraction of oxide; n is the refractive index of compressed powder (tablet); n_1 is the refractive index of oxide; $N_2=n_{met}-ik_{met}$ is the refractive index of metal (aluminum); i is the imaginary unit of a complex number; and k_{met} is the absorption coefficient of metal. By plotting the experimental points on the calculated nomogram, the thickness and volume fraction of metal in the tablet can be determined.

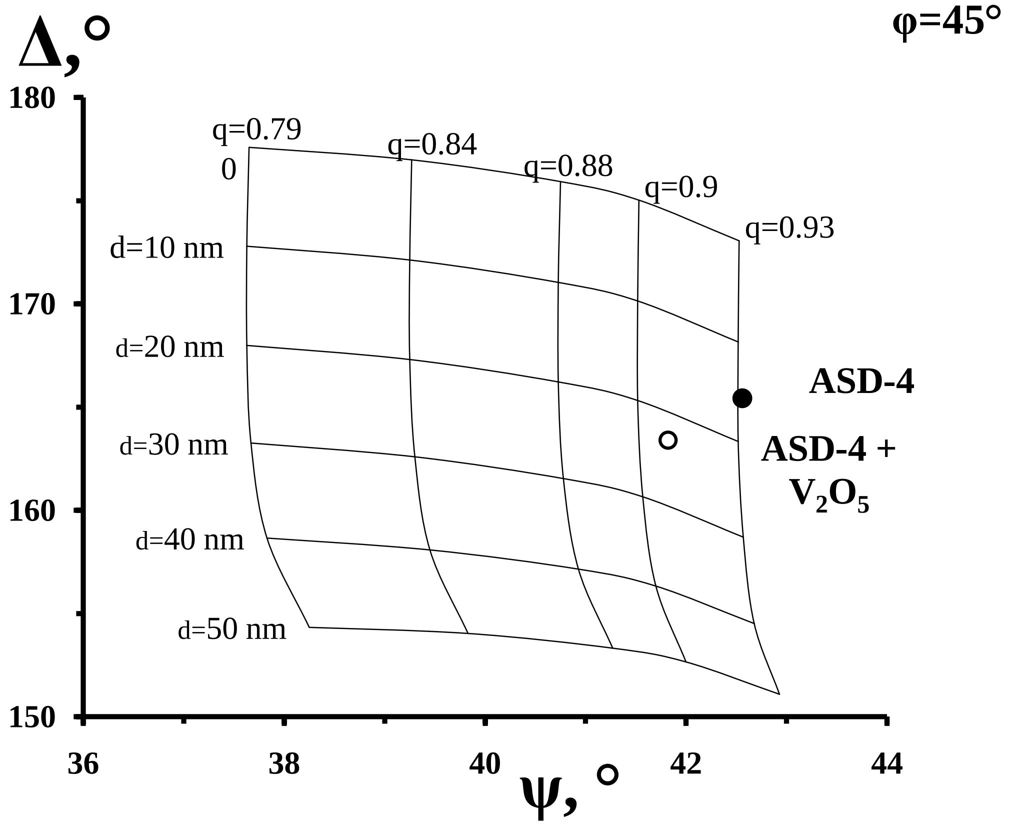

FIG. 4. The nomogram Δ-ψ for determining the thickness of the oxide film and the metal fraction in the compacted powder during oxidation, the angle of beam incidence is φ = 45°

Thus, for the initial ASD-4 powder, the average thickness of the oxide film was 16 ± 5 nm, which is in good agreement with the literature data [13], where the average thickness of the oxide film of ASD-4 particles is 17.9 nm. For ASD-4 + V_2O_5 powder, the average thickness of the modified layer (oxide + V_2O_5) was slightly higher, ~24 ± 5 nm. From formula (1) it is seen that only refractive indices of aluminum (n_{Al} = 1.65) and aluminum oxide (n_{Al2O3} = 1.6) were taken into account in the calculation of the nomogram, while the optical constants of the xerogel V_2O_5 and the porosity of the tablet were disregarded to simplify the calculations. In this connection, there is a certain error in determining the values of d and q for the modified powder. However, this method makes it possible to reliably retrace the oxidation kinetics of the modified powder and compare this process with the oxidation of initial ASD-4.

Based on the geometric characteristics of the ASD-4 particles [13], the densities of aluminum, Al_2O_3 and V_2O_5 oxides (ρ = 2.7, 3.99, 3.357 g/cm^3, respectively) and also assuming that the layer of $V_2O_5 \cdot nH_2O$ xerogel is the outer shell covering the ASD-4 particle and not interacting with it, it is possible to calculate the thickness of this shell if the content of metallic vanadium in the modified powder is 0.8 wt.%. Ideally, the thickness of this shell is equal to:

$$d_{V_2O_5} = \sqrt[3]{\frac{3(V_{ASD-4} + \frac{m_{V_2O_5}}{\rho_{V_2O_5}})}{4\pi}} - r_{ASD-4} = 19.4nm, \tag{2}$$

where V_{ACD-4}, r_{ACD-4} are the volume and the radius of ASD-4 particle, and mV_2O_5 is the mass of the xerogel shell calculated from the molar mass of the oxide and the mass content of vanadium in the sample.

Hence, the total thickness of the modified layer will be 35-37 nm, which is close to the value obtained by electron microscopy (40 nm). However, as seen from the microphotographs (Fig. 3), the real surface of the modified particles has a much more complex relief, which allows us to speak of some effective thickness of the modified layer.

It should be noted that ellipsometric measurements were carried out on compressed powders, where the core and the surface film of the particles are mechanically deformed. In this connection, such geometric parameters as the average thickness of the surface film of pressed particles may differ from freely poured powder.

Thus, the obtained data on the surface of modified powders are indicative of the formation of a layer with a well-developed nanorelief and high adhesion caused by the possibility of intercalation of vanadium oxide xerogel with aluminum ions, its thickness is within 24-40 nm. These factors provide the powder with a combination of high rheological characteristics, storage stability in air and at the same time high energy characteristics due to close contact of the modifier with the particle surface.

IV. CONCLUSION

Using ellipsometry, microscopy and elemental analysis, it was shown that the samples, obtained by impregnation of aluminum powder with vanadium-containing hydrogel, after drying and calcination at 623 K in air represent a system, in which the deposited gel forms a nanosize layer impregnated with $V_2O_5 \cdot nH_2O$ on the particle surface. If the content of metallic vanadium in the modified powder is 0.8 wt. %, the surface layer is characterized by a highly developed relief with good adhesion due to the chemical bonding of the modifier with the surface of aluminum particles owing to the intercalation of aluminum ions in the xerogel structure.

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