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Multifunctional composite coatings on Al and Al alloys

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nelan
oxide
plus

Welcome to Karelia!

Research Laboratory
“Physics of Nanostructured Oxide Films & Coatings”

Objects

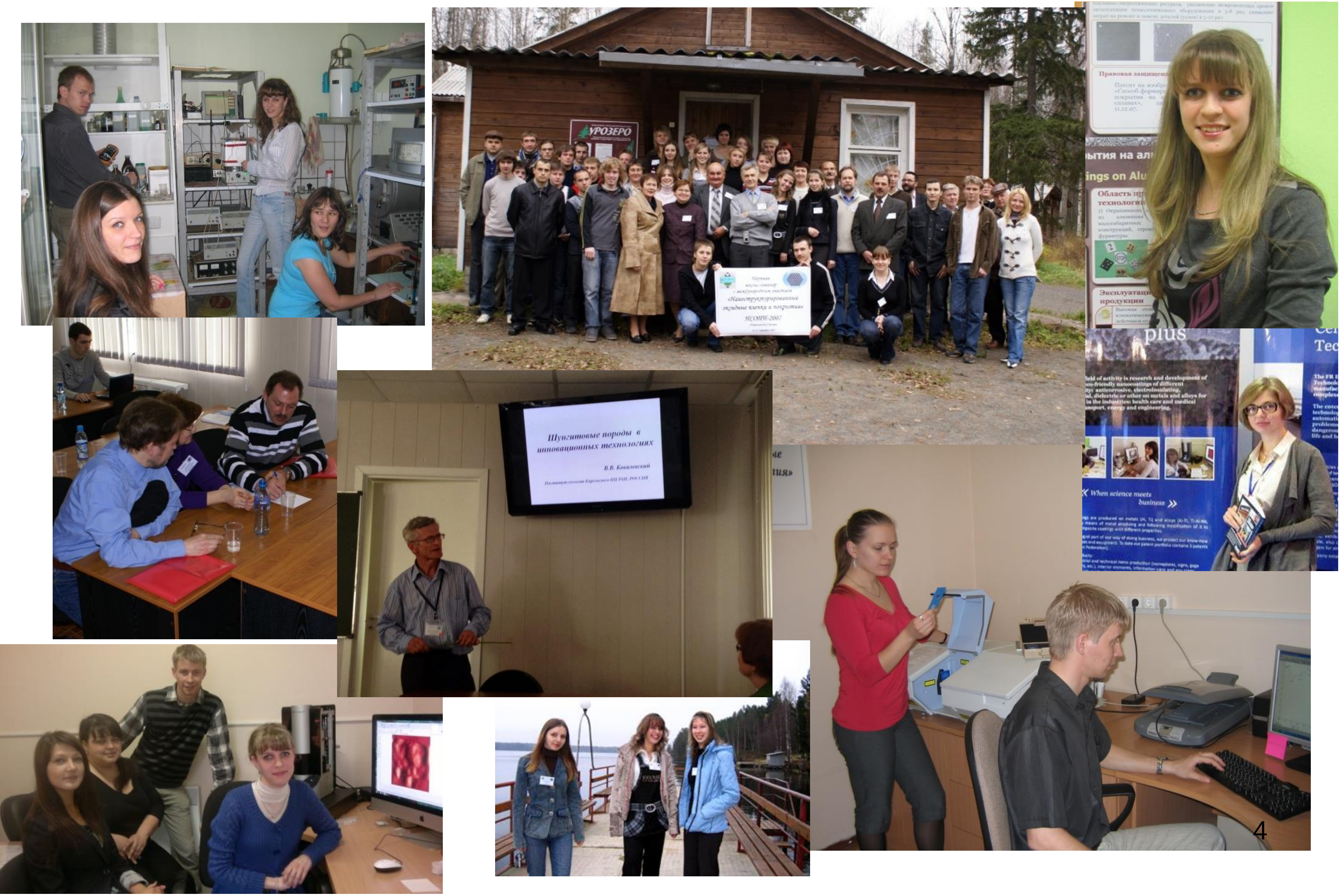
✓Anodic oxide films formed on different metals (Al, Ti, Nb,Ta) and alloys (Ti-Al, Ti-Al-Nb, Al-Mg). We have a particular interest in nanoporous and nanotubular anodic ***aluminas & titanias***.

Research Areas

✓The main field of activity is research and development of advanced eco-friendly nanostructured coatings of different functionality.

✓Investigation of the principles of formation of self-organized porous and tubular anodic oxide films on the base of analysis of their ***structure on different scales: atomic, mesoscopic and microscopic (by means of XRD, TEM&SEM, AFM, FTIR)***.

Research Laboratory
“Physics of Nanostructured Oxide Films & Coatings”

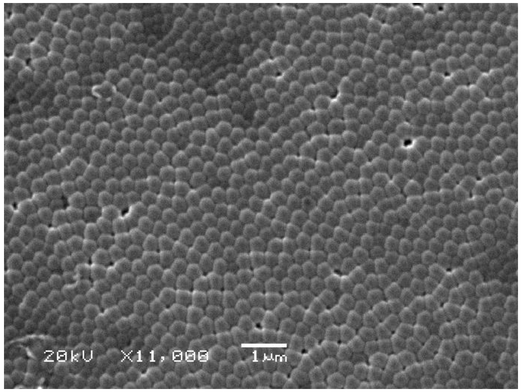


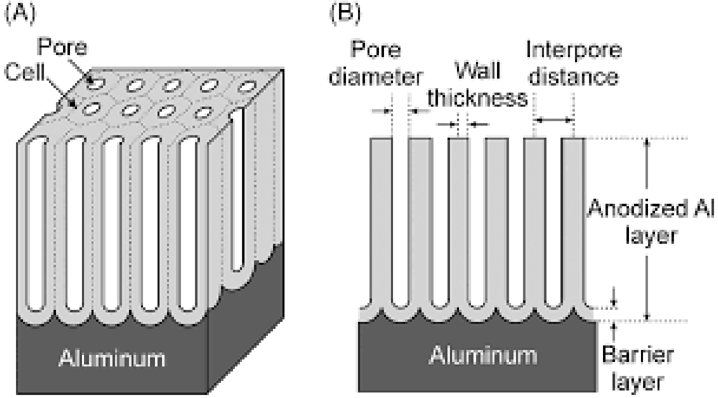
Introduction

✓Electrochemical oxidation of metals in electrolyte solutions, or anodizing, been successfully used for many years for producing films and coatings of different functionality.

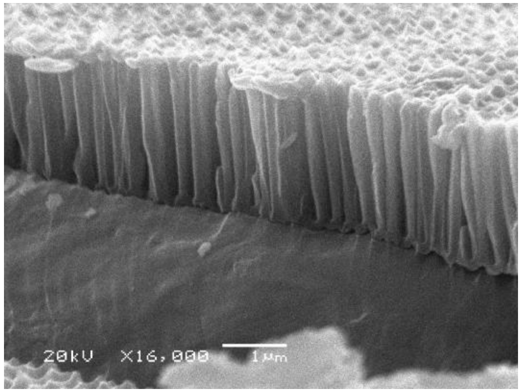
✓Only anodizing allows you to create on the surface of some metals self-organized metal oxide films, which are characterized by the presence of regularly arranged pores/tubes of nanosized diameters.

✓The most studied object is the porous anodic alumina. Pores array formation occurs under synergy of oxide film growth and dissolution processes that is implemented in many acid solutions.





Idealized structure of porous anodic alumina (A) and a cross-sectional view of the oxide layer (B).

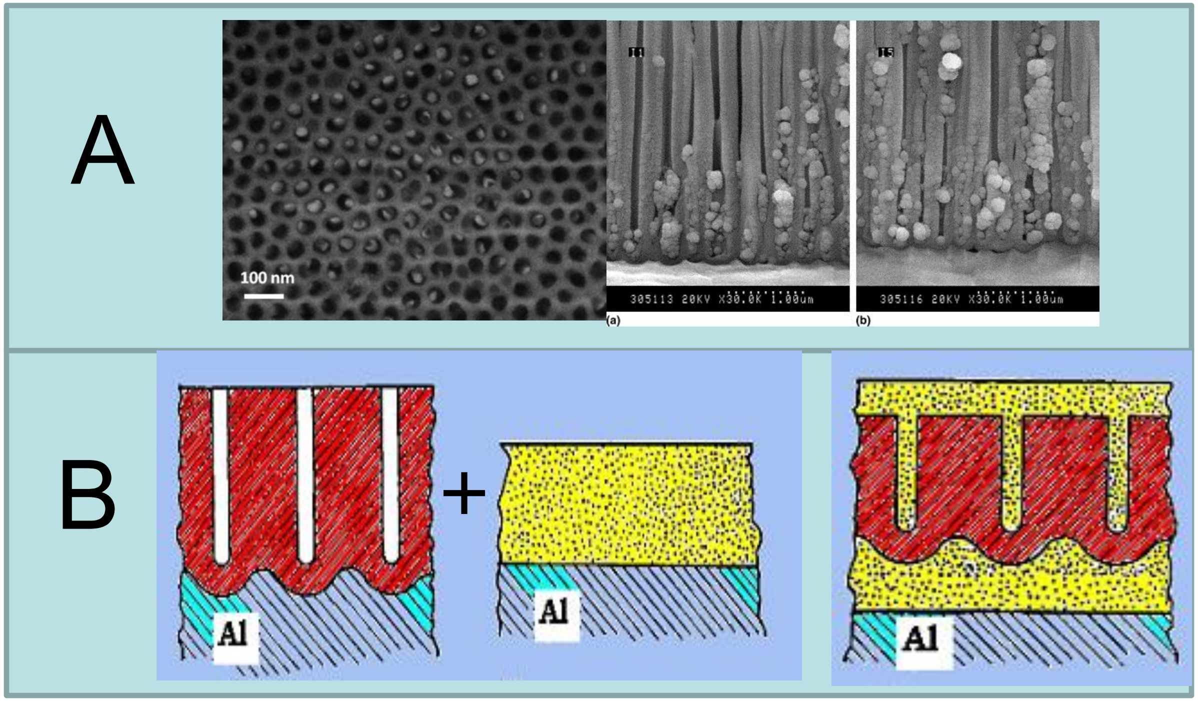


Introduction

✓It seems tempting to expand the range of porous alumina functional properties by means of further modification.

✓A number of such methods is known, among them (A) - doping with nanoparticles of metals and metal oxides and (B) - re-anodizing of porous oxide for partial filling of pores with barrier type oxide*.

Composite nanostructured coatings on the base of porous anodic alumina



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* Yakovleva N.M., etc. *Thin Solid Films,* 2000, Vol. 366, pp. 37-42.

Aim of this work

(i) to summarize our data on fabrication of self-organized porous oxide films via anodizing of Al and Al alloys;

(ii) to report on development of the multifunctional composite coatings* by two-step anodizing of Al and aluminium alloys;

(iii) to report on development of the catalytic nanocomposite coatings by modification of self-organized alumina matrix with MnO_2-nanoparticles.

*The *multifunctional* composite coatings – composite coatings capable of withstanding *simultaneously* the effects of high voltage, radiation background, corrosive environment, high temperatures, humidification, etc.

Objects & Methods

✓ Porous anodic alumina (PAA) formed on high purity Al (A99) and Al alloys (AA1050, AA1230) in water solutions of 3 - 5% $C_2H_2O_4$ and multicomponent electrolyte (MCE)*.

✓ Anodic aluminas formed by conventional anodizing technique and two - step anodizing techniques:

(i)1st step – porous anodizing; 2nd step – re-anodizing (Ua= 300-1200V) in barrier type electrolyte (4 g/l H_3BO_3);

(ii) 1st step – porous anodizing in 5% $C_2H_2O_4$; 2nd step –anodizing in MCE (after oxide removal).

✓ γ-MnO_2nanoparticles were got by thermal decomposition of 5% $KMnO_4$ water solution**.

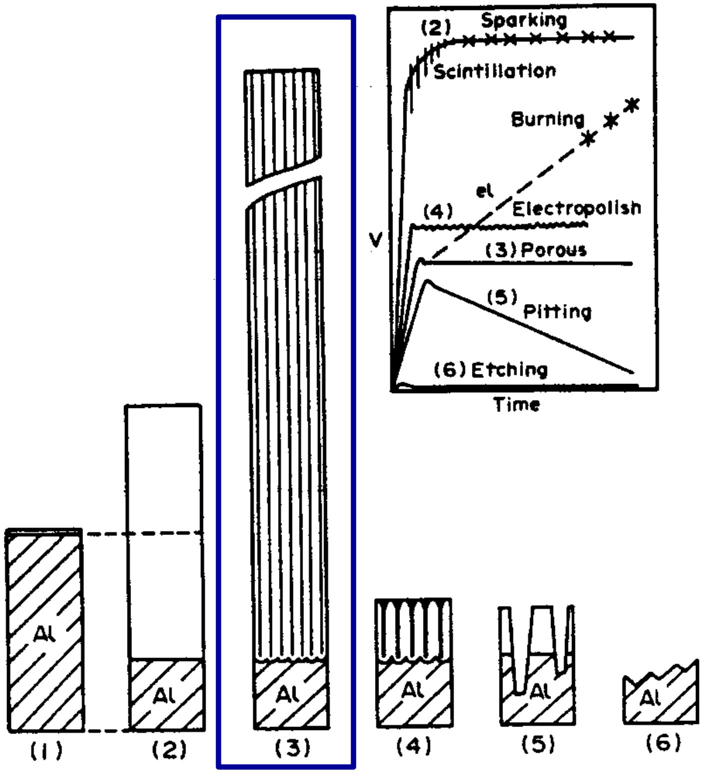
✓ Objects were characterized by means of transmission and scanning electron microscopy (TEM&SEM), atomic force microscopy (AFM), X-ray diffraction (XRD).

✓ Catalytic tests of the produced composite structures in the model reaction of oxidation of CO into CO_2 were carried out using a *BI-CAT flow4.2(A)* universal flow-type installation

*MCE: 50 g/l $C_2H_2O_4$+10 g/l $C_6H_8O_7$+50 g/l H_3BO_3+100 ml/l C_3H_8O;

**Kokatev A.N., etc. *Protection of Metals and Physical Chemistry of Surfaces, 2016, Vol. 52, No. 5, pp. 832–838.*

Aluminium Anodizing



Five types of voltage-time curves for the anodizing of Al at constant current density may be identified*.

✓Depending on anodizing process conditions the thickness and properties of the anodic oxide films (or anodic coatings) of aluminium will vary in a large scale.

✓If the formed alumina is weakly dissolable in the electrolyte, then porous anodic alumina (PAA) will form(3).

✓Controlling parameters:
Electrolyte, Voltage, Temperature, Time
Cell size D(nm) ~2.5×U_a(V)
Pore size d(nm) ~U_a (V)

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*Tajima S. Adv.Cor.Sc.&Techn. V.1.P.229.1970

Porous anodic alumina (PAA)

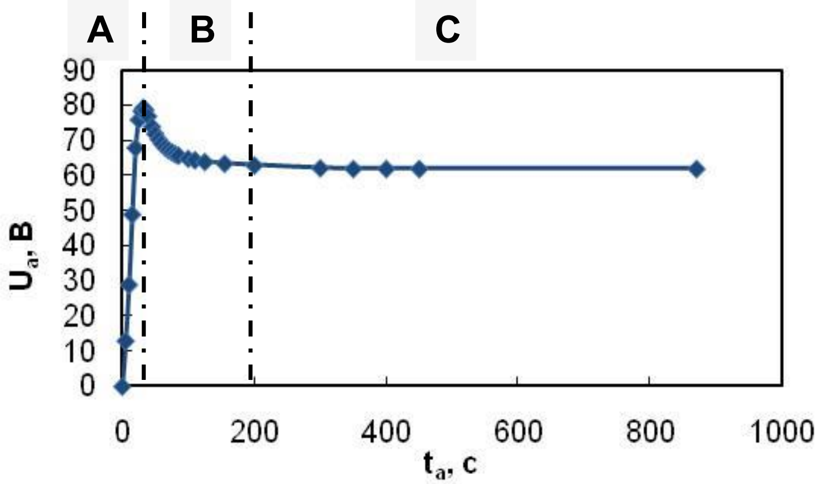
Conventional anodizing

- ✓ Electrolytes

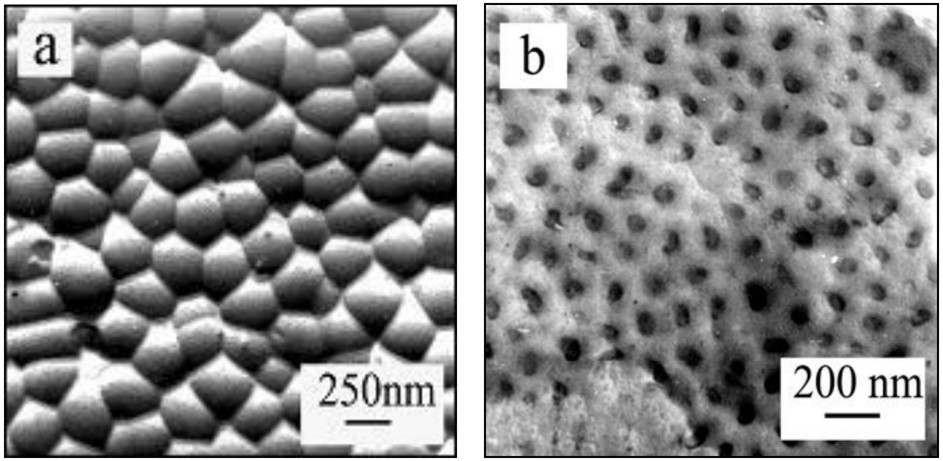
Water acidic solutions
(3-5% $C_2H_2O_4$, 1% H_3PO_4 and 20% H_2SO_4).

- ✓ Regimes

Voltstatic regime (VSR) ➡ U_a=const;
Galvanostatic regime(GSR) ➡ j_a=const.



U_a(t) -curve for GSR anodizing of Al in 3% $C_2H_2O_4$, T_a=15^{o}C, j_a = 1 A/dm^2.

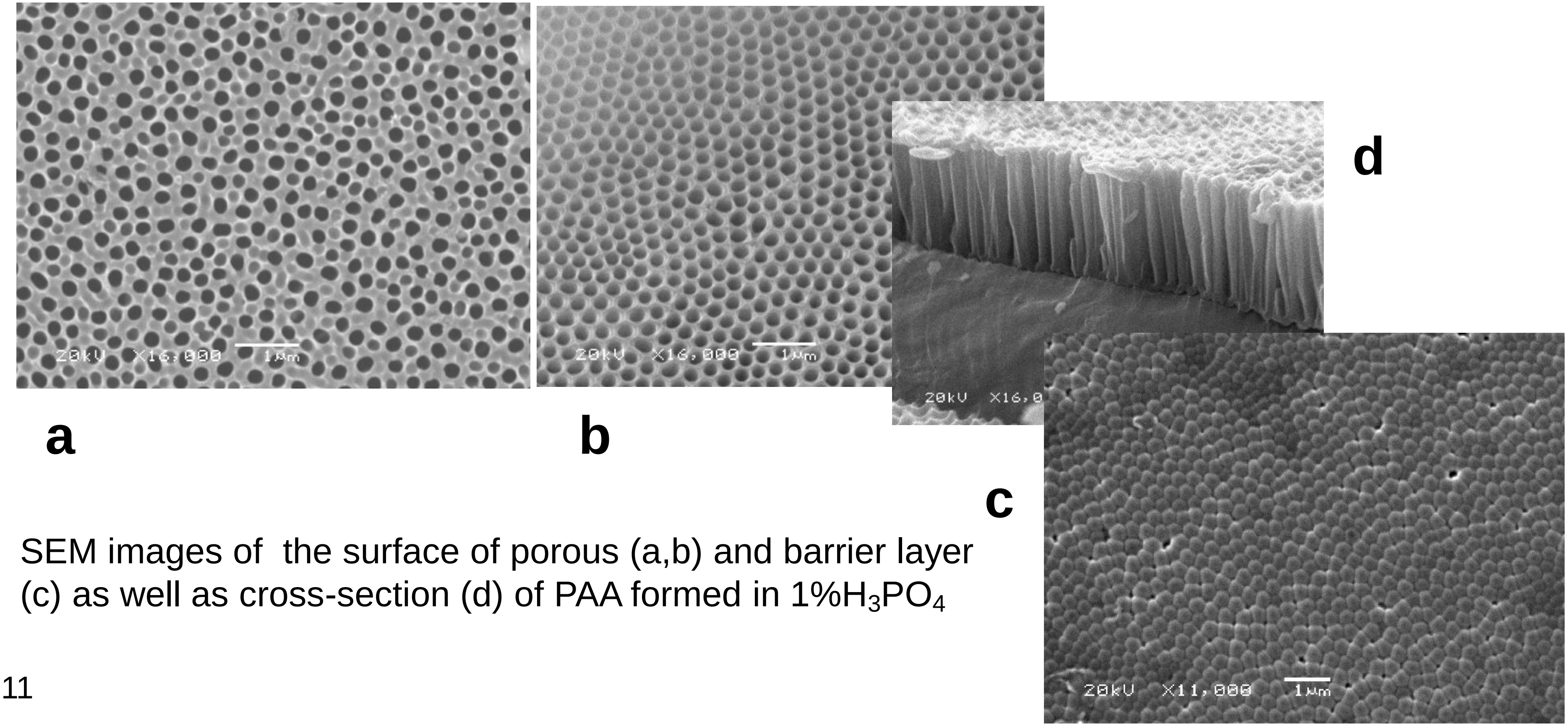


TEM images of barrier (a) and porous(b) layers surfaces of PAA formed in 3% $C_2H_2O_4$.

✓Effective pore diameter: $<d_p>=(15\pm5)$nm (20% H_2SO_4), $<d>=(65\pm20)$nm (3% $C_2H_2O_4$).

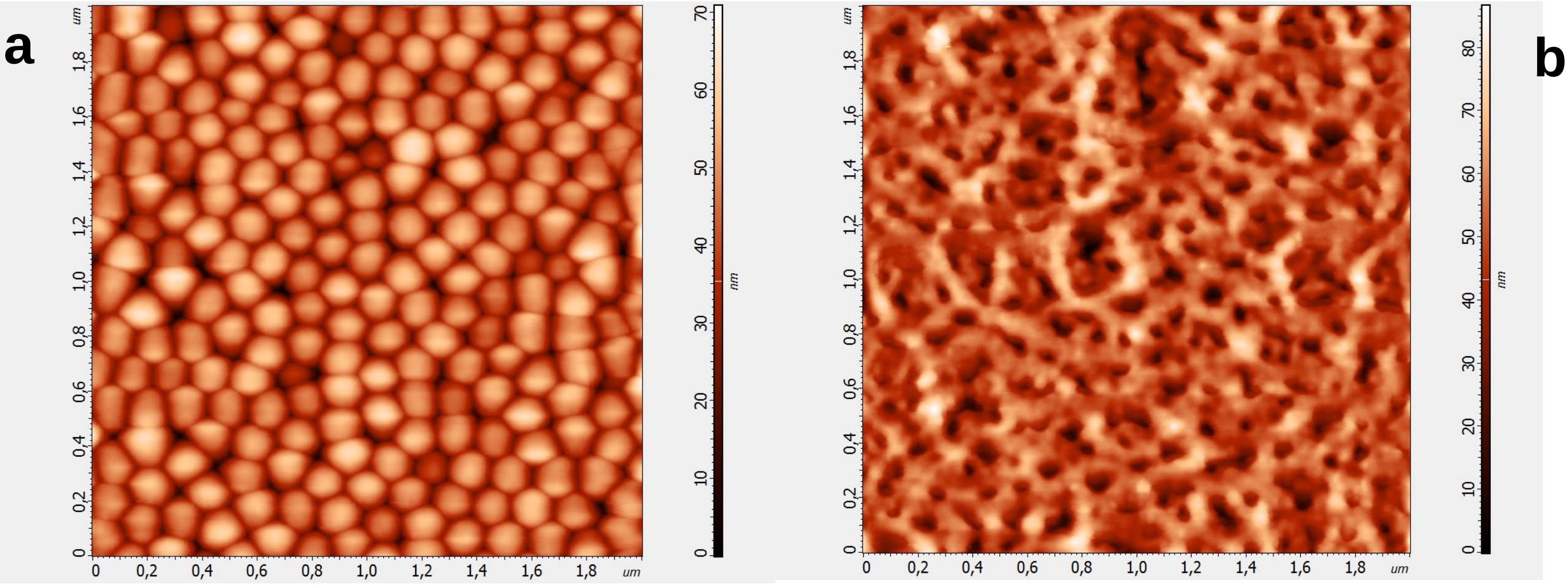
Mesoscopic-scale structure of PAA

- ✓ Mesoscopic-scale structure characterizes the mutual arrangement of cells or pores/tubes on the oxide surface.
- ✓ Conventional anodizing of Al and Al alloys provides the formation of nanostructured oxide films with amorphous mesostructure.
- ✓ Anodization of Al in special conditions of self-organized growth leads to formation of PAA with a polycrystalline mesostructure.



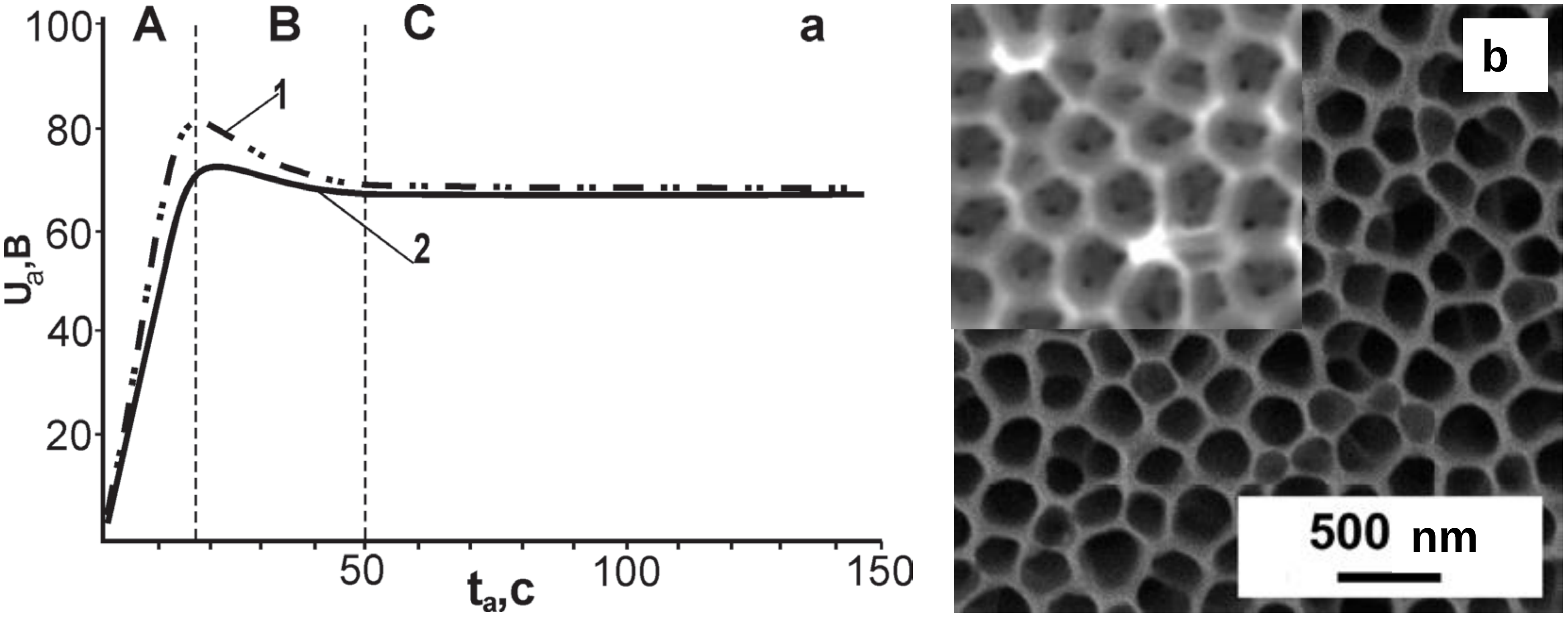
SEM images of the surface of porous (a,b) and barrier layer (c) as well as cross-section (d) of PAA formed in 1%H_3PO_4

Conventional Al anodizing



AFM images of barrier (a) and porous (b) layers of PAA formed in 5% $C_2H_2O_4$, j_a=25mA/cm^2 , t=30 мин (δ = 25 μm).

Highly ordered porous anodic alumina

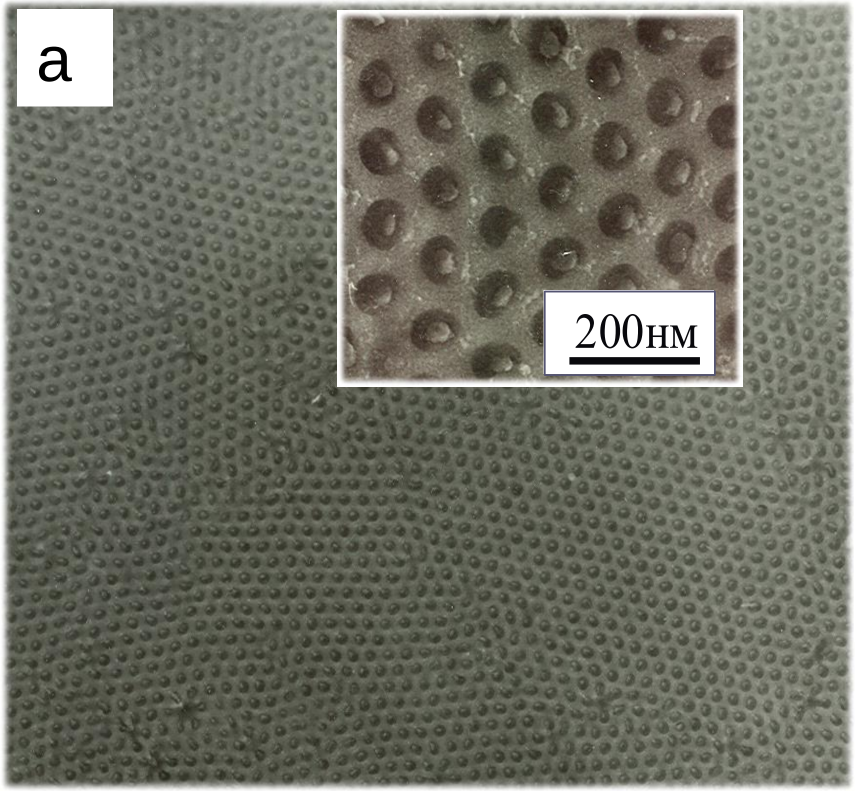


$U_a(t)$ curves for two-step GSR anodizing of Al in 3 % $C_2H_2O_4$ - (a). A, B, C — stages of anodic porous oxide development. SEM images of PAA porous layer surface - (b).

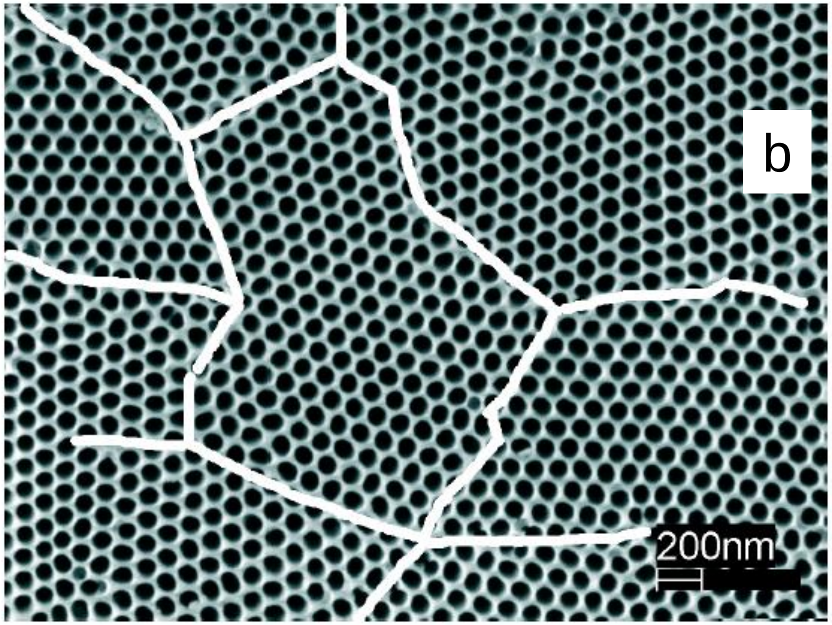
Scheme of two-step anodizing process

Polycrystalline mesoscopic structure of PAA

✓Anodization of Al in special conditions of self-organized growth leads to formation of PAA with a polycrystalline mesostructure.



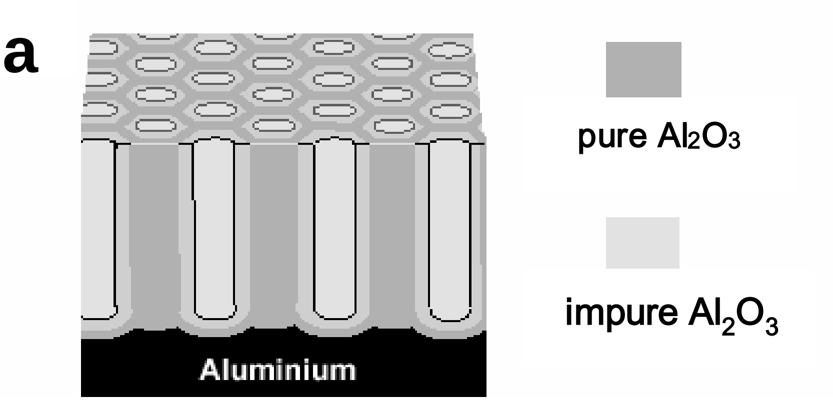
TEM-image of the surface of PAA formed on Al in 3% oxalic acid solution (U_a=40V) (a).

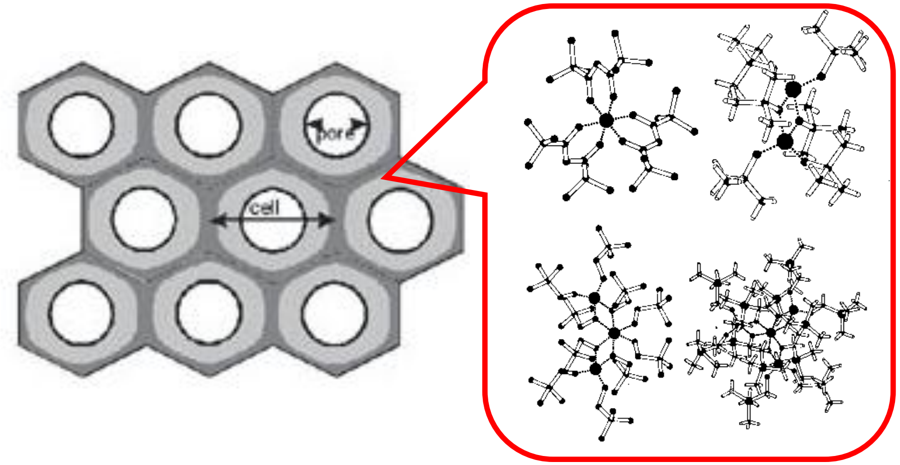


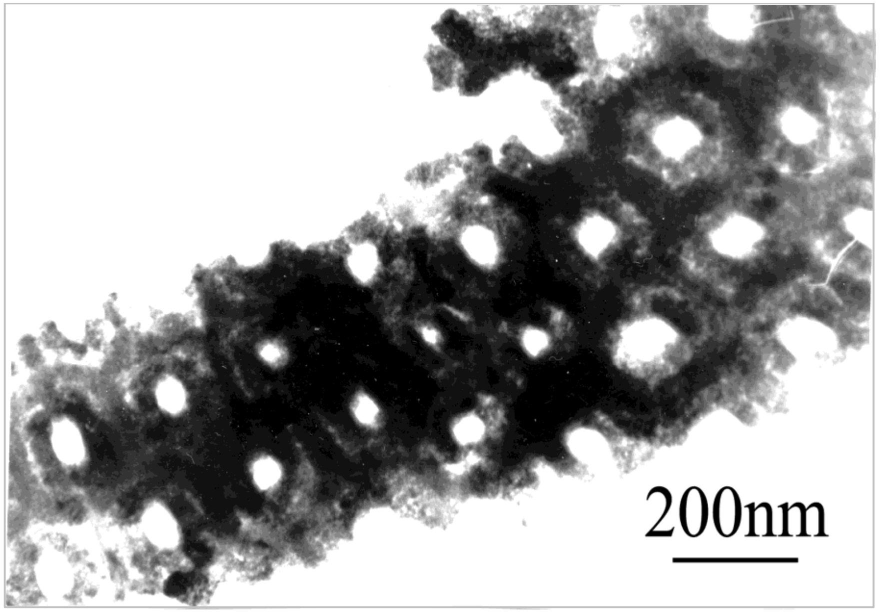
SEM image in which some of the “grain boundaries” between the ordered domains in PAA have been highlighted (b).

Morphology of PAA

- Main feature of PAA is structural heterogeneity. There are two different regions in PAA: relatively pure alumina and anion-contaminated alumina.
- Forming mechanism of anion-contaminated region of PAA is defined by the alternation of field-stimulated oxide dissolution and deposition of colloidal anion-contaminated oxide nanoparticles according to sol-gel process.

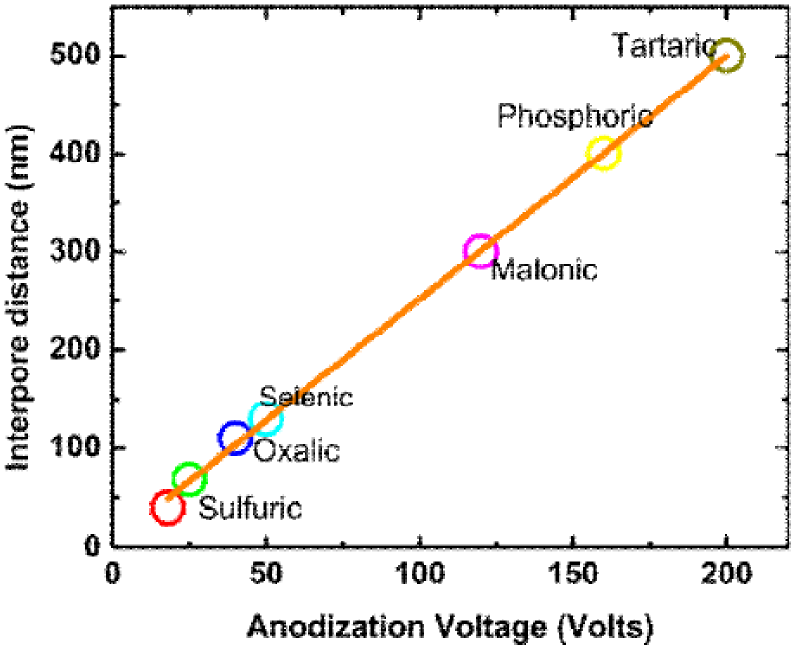


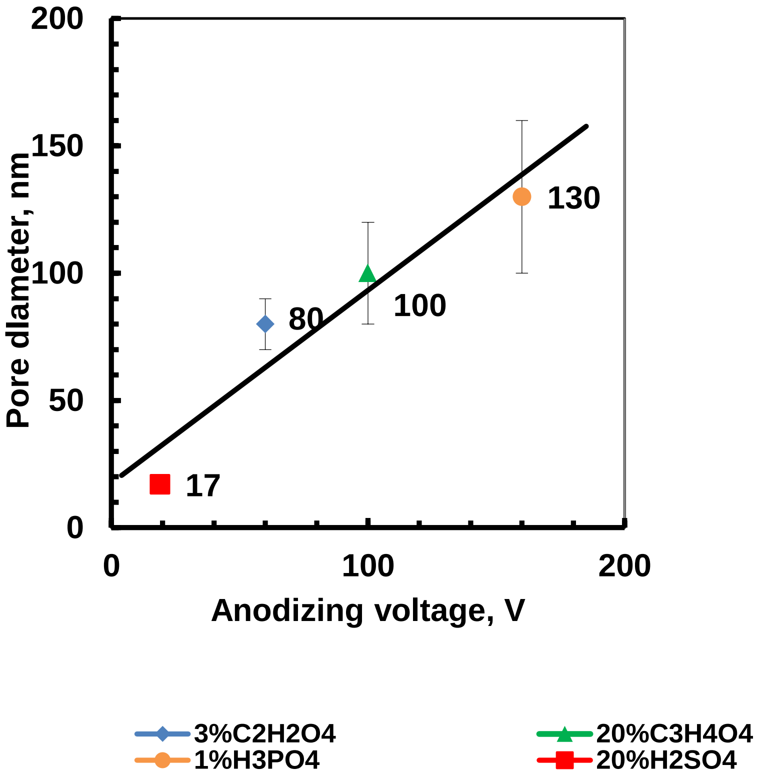




TEM-image of the fragment of PAA, formed in 3%$C_2H_2O_4$, after annealing under T=1323 K

Highly-ordered PAA



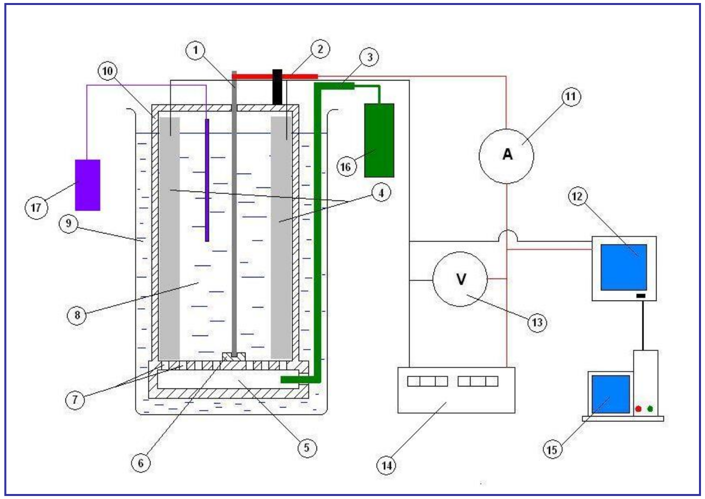


- ✓ Oxide layer thickness is 10 to 100µm thick.
- ✓ Pore size $<d_p>$ =(15-160) nm.
- ✓ The choice of anodizing technique is dictated by definable pore size and the required oxide thickness.
- ✓ The first parameter is determined by the process voltage, and it, in turn, by the choice of anodizing electrolyte, and the second parameter – by the time of anodizing.

Two-step anodizing technique to fabricate of multifunctional composite coatings on Al operated in extreme conditions

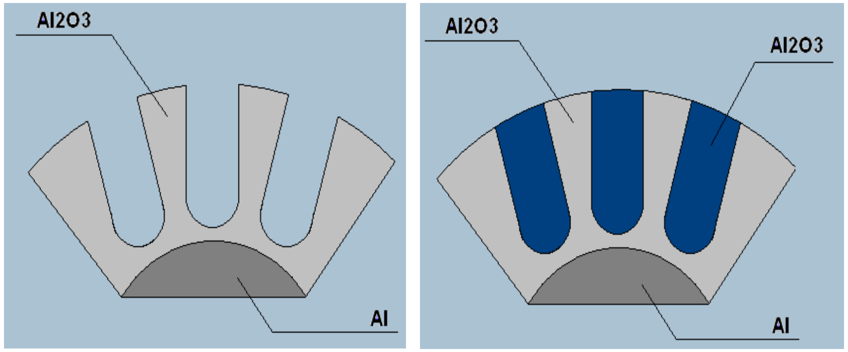
✓In the present work we apply the special two-step anodizing (TSA) technique (the 1st step is anodizing of Al in multicomponent electrolyte, the 2nd step – in boric acid electrolyte) to formation of electric insulating oxide coatings on pure unpolished Al and some Al alloys.

The samples were made from Al foil (A99) and wire (AA1230) after TSA anodizing.



Experimental anodizing set-up.

Oxide film morphology



Two-step anodizing scheme

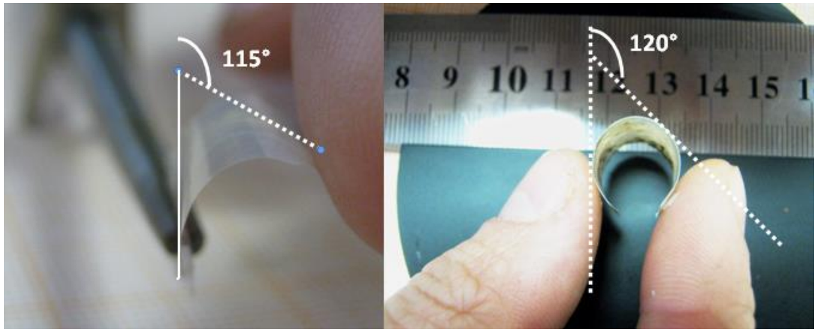
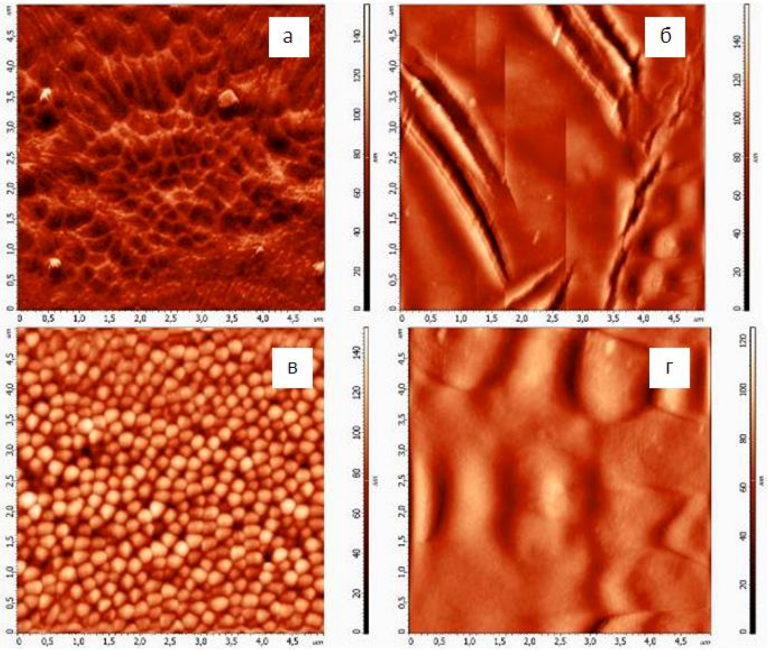


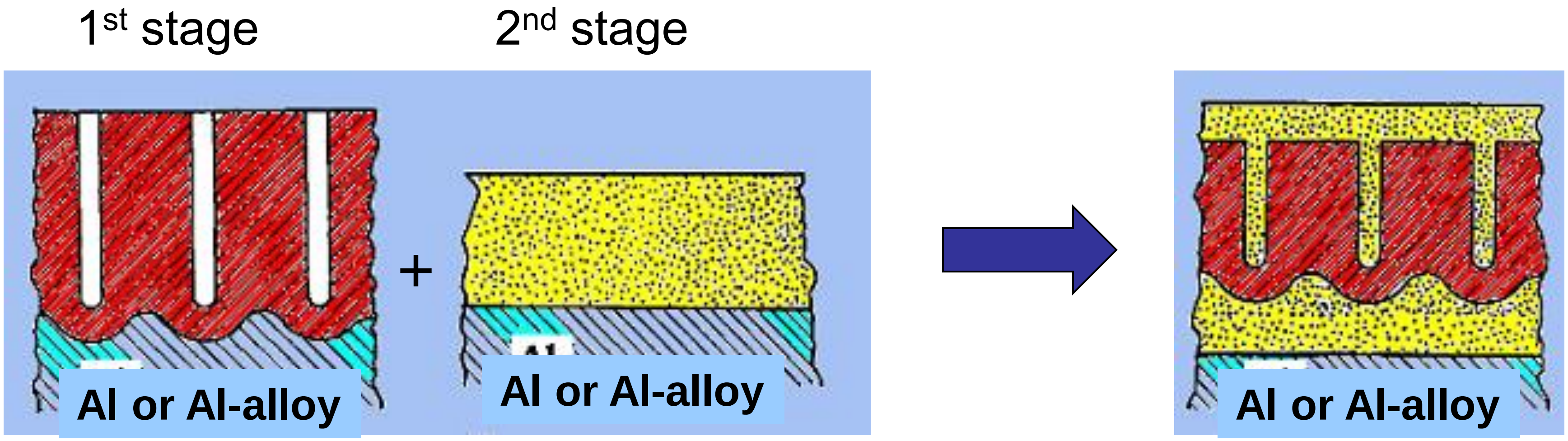
Illustration of oxide flexibility of PAA formed in MCE



AFM images of porous film surface (a-porous layer surface; b- barrier layer surface), formed after 1st step in MCE and TSA- film surface (c- outer oxide surface, d- inner oxide surface). Anodizing of Al wire (AA1230). Re-anodizing under Ua=1200 V.

After the 2nd stage smoothing of Me-Ox interface takes place. Cells aggregate in elements of ~ 0.5 – 1.0 μm size. Optimal porous oxide thickness 50-60 μm and resulting coating thickness is 40-50 μm.

Composite structures formed by two-step anodizing of Al and Al alloys



1st stage – porous anodizing, δ_1=10 μm.

2nd stage – high-voltage anodization (Ua=1200-1500V) in barrier type electrolyte, $\delta_2 \approx$5 μm.

As a result of high-voltage anodization of porous oxide film it is filling the pores and obtaining of dense-like oxide coating.

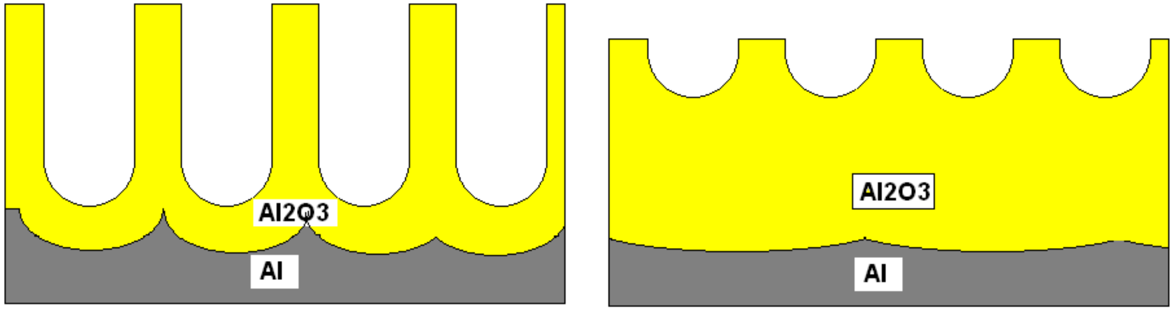
Two-step anodizing of Al and different aluminium alloys allows us create electroisolating coatings, which guarantees breakdown voltage on direct current up to 3kV under normal conditions and 1kV under high humidity conditions.

Composite structures formed by two-step anodizing of Al and Al alloys

✓It was established, that during re-anodizing of porous films more than 30 μm thick, full transformation of porous oxide does not take place, coating properties are defined by “quasibarrier” layer, as well as by porous upper layer.

1^{st} stage

$\delta_1 \approx 48$ μm



2^{nd} stage
Ua=1200 V

$\delta_2 \approx 43$ μm

✓These coatings can exploitable at influence of high temperature, increased radiation background, corrosive medium as well as high humidity.

✓So these coatings are multifunctional coatings because they are capable of withstanding *simultaneously* the effects of high voltage, radiation background, corrosive environment, high temperatures, humidification, etc.

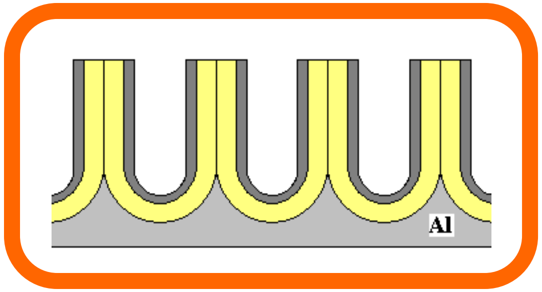
✓It was found, that given the coating thickness from 30 to 50 μm it can withstand voltage on alternative current up to 2.5 kV.

Composite structures on the base of PAA

✓Porous anodic alumina with high specific surface area can be used as matrix for deposition of catalytically active compounds and particles, i.e., a basis for creating composite coatings with catalytic properties.

✓It prevents from their aggregation and protects from external influences. In addition, it allows to construct highly ordered composite structures.

✓The subjects of our investigation are composite structures obtained by fabrication of MnO_2 nanoparticles inside PAA pores.



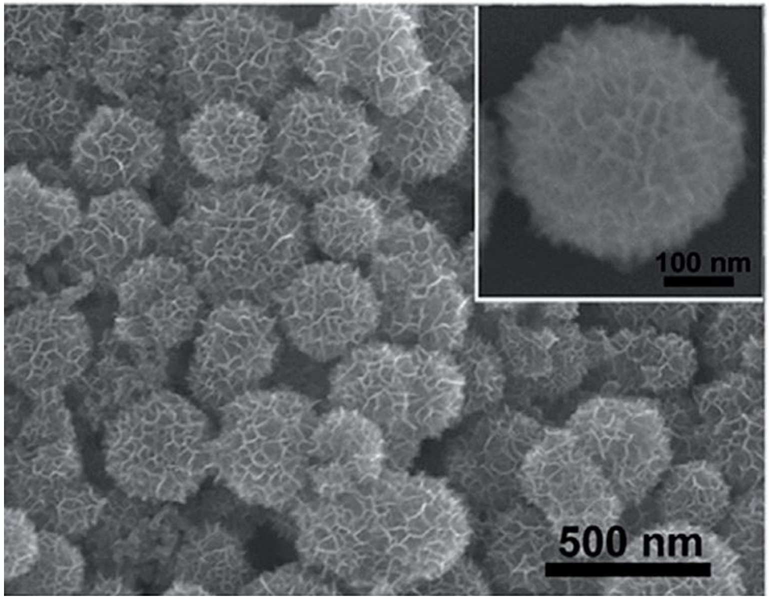
1st stage: Al anodizing

2nd stage: Modification of porous layer by MnO_2 nanoparticles

Why MnO_2 nanoparticles ?

✓Mesoporous manganese dioxides (for example γ-MnO_2) are active catalysts of oxidation of various volatile organic compounds (for example, **formaldehyde***), which is facilitated by their high specific surface area.

✓In view of the above, application of “ultradispersed γ-MnO_2/nanoporous Al_2O_3/Al composites appears to be promising in the development of catalytic systems.

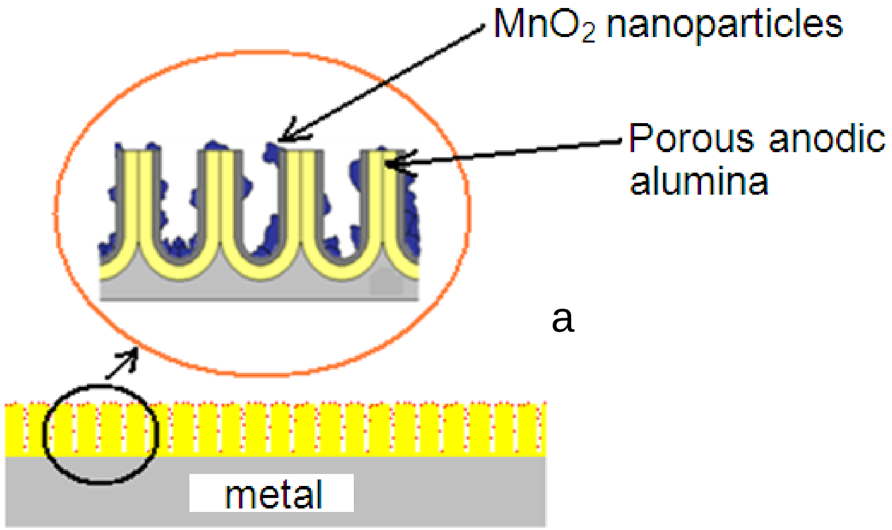


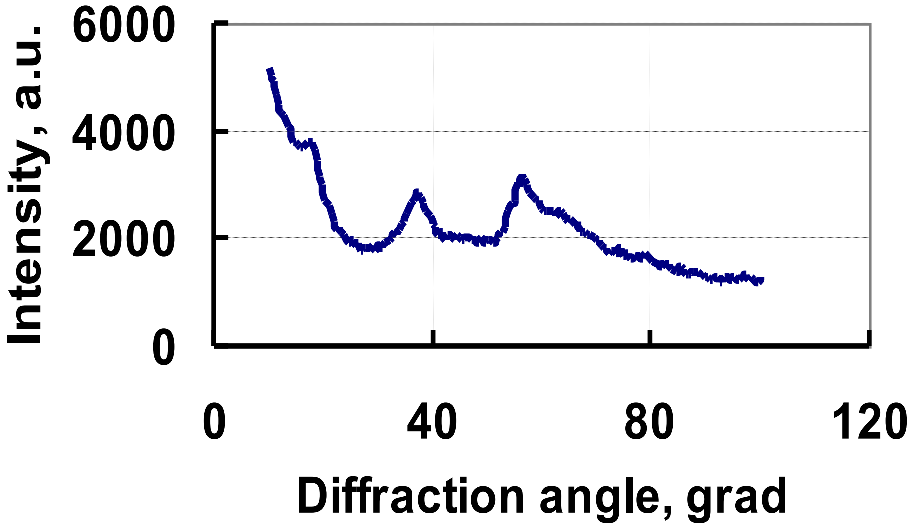
SEM images of mesoporous γ-MnO_2**.

*Bai B.,etc. Chin. J. Catalysis 37 (2016) 27–31

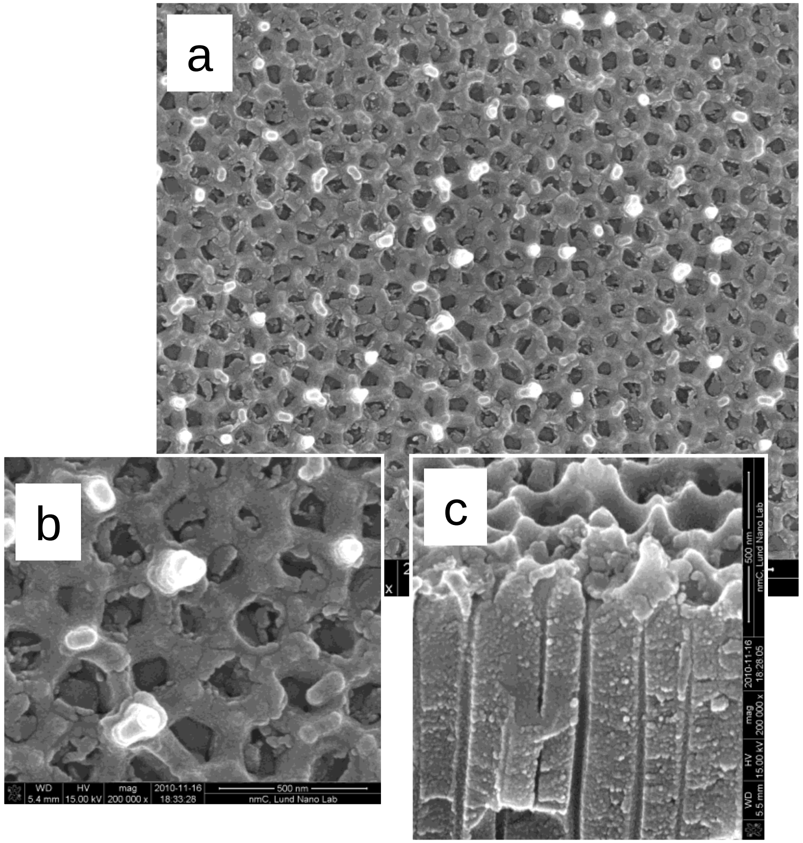
**Chen C.-H., Suib L. J.Chin.Chem.Soc. 59(2012)1-9.

Composite structures with ultradispersed MnO_2



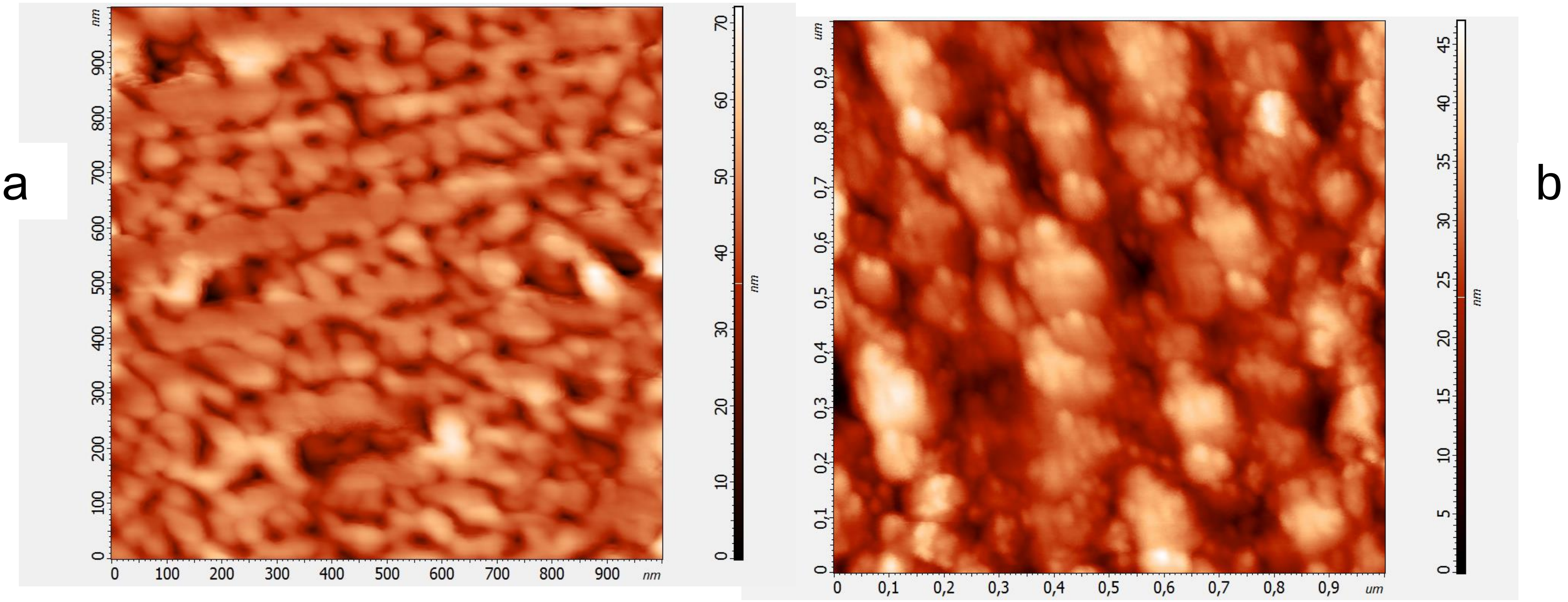


The X-ray scattering intensity curve for ultra-high dispersed heat-resistant MnO_2

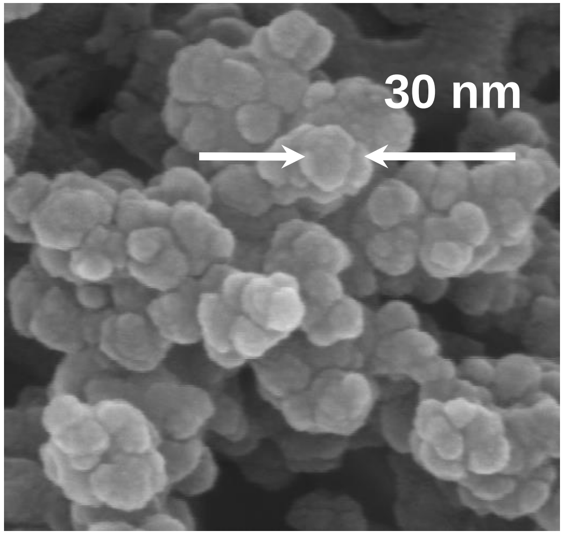


SEM images of the porous layer surface (a,b) and cross section (c) of PAA formed in 3%$C_2H_2O_4$ after deposition of ultradispersed MnO_2.

Composite structures with ultradispersed MnO_2



AFM images of porous layer surface before (a) and after (b) MnO_2 deposition (thermal decomposition of potassium permanganate: 5% solution of $KMnO_4$, 5 min, 20–230°C, 3 cycles*.



SEM-image of the matrix surface after deposition of γ-MnO_2

Kokatev A.N., etc. *Protection of Metals and Physical Chemistry of Surfaces, 2016, Vol. 52, No. 5, pp. 832–838.*

In conclusion…

✓To sum up, it has been demonstrated that application of the reaction of thermal decomposition of potassium permanganate under the suggested conditions enables one to obtain thermally stable ultradispersed γ-MnO_2 on the surface of the nanoporous anodic aluminum oxide.

✓The samples modified with manganese dioxide catalyze the reaction of oxidation of CO into CO_2 at temperatures above 180°C. The concentration and surface distribution of γ-MnO_2 particles depend on the morphological structure of the porous aluminum oxide determined by the anodizing conditions.

✓The produced “ultradispersed γ-MnO_2/nanostructured Al_2O_3/Al” catalytic systems may prove efficient for the removal of carbon monoxide and other gases hazardous for human health from the air due to a combination of high specific surface area of the self-organized oxide matrix and catalytic activity of manganese dioxide nanoparticles.

Thank you for your attention!

Contact info
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Каталитические испытания

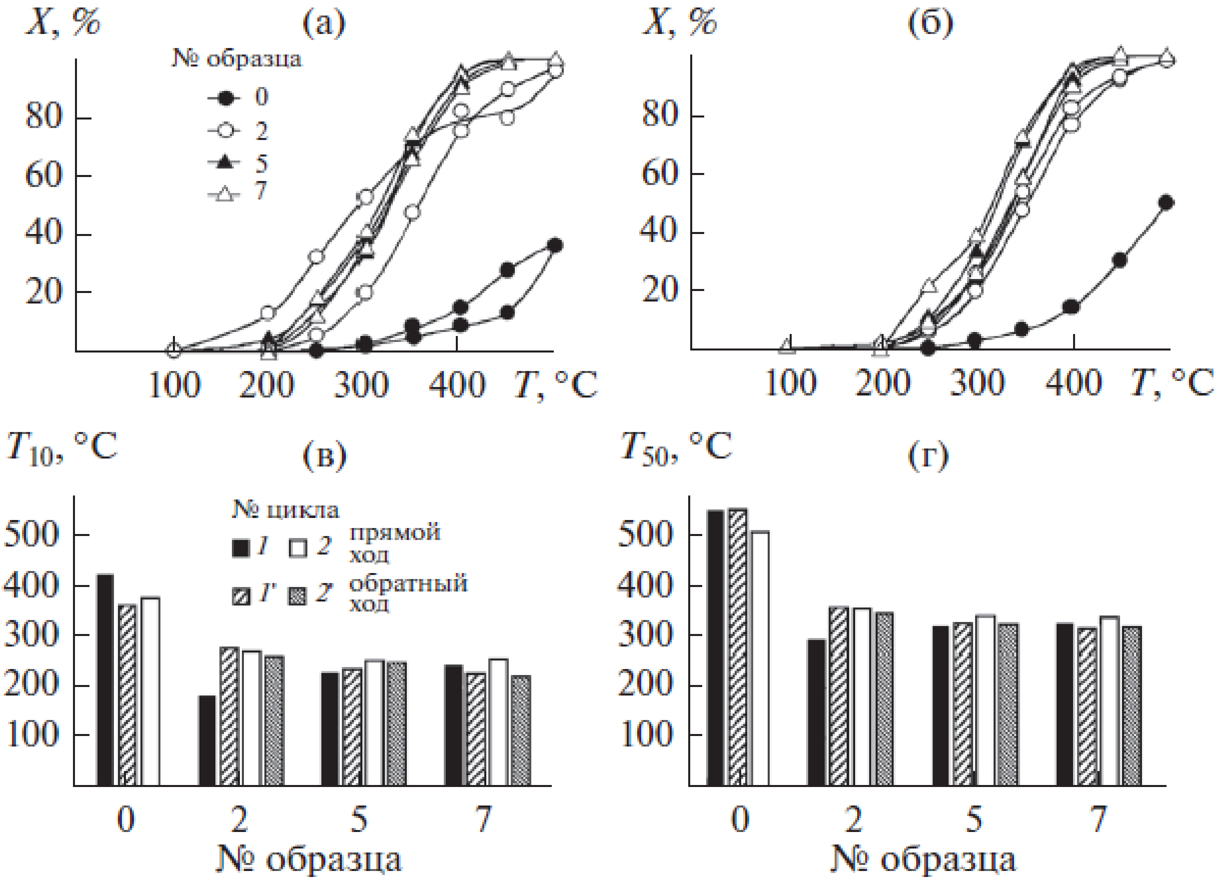

Рис. 5. Температурные зависимости конверсии CO (*X*, %) в первом (*а*) и втором (*б*) циклах каталитических испытаний, температуры начала конверсии T_{10} (*в*) и полуконверсии T_{50} (*г*) для образцов: анодированной фольги-1(0) и модифицированной диоксидом марганца анодированной фольги-1 (2) и фольги-2 (5, 7).