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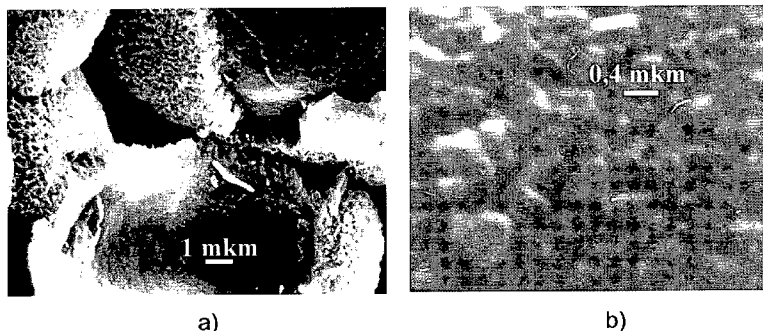


Fig. 1.

(57) Abstract: This invention is related to the field of synthesis of porous composite metal-ceramic materials including both porous and non-porous elements having various configurations and different chemical compositions and having a pore size ranging from  $\mu\text{m}$  to  $\text{nm}$ . A number of synthetic gas-and-fluid permeable composite materials in the form of a solid with a porous- 0 open structure of crystallite aggregates of aluminum hydroxide  $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$  or alumina ( $\text{Y-Al}_2\text{O}_3$ ) coupled by phase contacts are achieved due to said material made with the specific surface from 50 to 200  $\text{m}^2/\text{g}$ , while the space between said crystallites presents pores having a diameter from 4.5  $\text{nm}$  to 100  $\mu\text{m}$  and said material is synthesized by the dissolution of disperse aluminum in an aqueous solution having  $\text{pH}=7.5-11.5$  at the maximum temperature of 1000C (preferably from 85 to 95°C) followed by the 5 mass crystallization of aluminum hydroxide from a supersaturated solution of aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts.

## POROUS COMPOSITE METAL-CERAMIC MATERIALS

## Description

## FIELD OF THE INVENTION

This invention is related to the field of synthesis of porous composite metal-ceramic materials including both porous and non-porous elements having various configurations and different chemical compositions and a pore size ranging from  $\mu\text{m}$  to  $\text{nm}$ .

## BACKGROUND OF THE INVENTION

Modern technologies make wide use of porous non-organic materials both of natural and synthetic origin. Synthetic porous non-organic materials at present are mainly produced by the methods of powder metallurgy (filters, capillary structures of heat pipes, aerators etc.) and by those of colloid chemistry (adsorbents, catalyst carriers). Despite the principal differences between the above approaches they are intended for one and the same purpose that is the production a solid with open through-pores and in a great number of cases with a globular structure presenting a coalescence of either porous or non-porous particles which are spaciouly positioned in a particular way and coupled by phase contacts. The size and configuration of particles as well as their mutual positioning form a structure of voids or pores which define structural properties of the material such as pore size distribution, effective pore radius, specific pore surface, liquid-and-gas permeability and other properties. A framework of the material comprised of particles connected in the contacting area defines the totality of its framework properties (size and state of contacts, mechanical strength, heat-and-electric conductivity, corrosion resistance etc.). The structural and framework properties of a porous material can be easily adjusted in a desired manner by varying a granulometric composition of particles and their mutual positioning and by controlling the formation of contacts.

Those skilled in the art of a porous material production very often find it necessary to combine a number of properties that are counter-dependent on the granulometric composition of particles. For example, high liquid and gas permeability is to be combined with high filtering capacity i.e. a small pore size, high specific surface with high permeability, high mechanical strength with high specific surface, corrosion resistance etc. The problem of producing the materials in question presumes an in-depth study of the production methods and primary materials and requires the application of new approaches to solve the material science tasks since the production of the above materials by conventional approaches is not possible as a rule.

The application of only conventional approaches characteristic of powder metallurgy such as forming and sintering usually fails to substantially improve the efficiency of permeable powder materials. In this connection there were developed and successfully applied various methods of a porous structure adjustment which are intended to improve the working properties of materials and those of end products. Below there are listed only some of the methods used to adjust a porous structure of permeable powder materials such as rolling and spheroidization of particles before forming, the deposition of fine particles or thin layers in porous media by means of passing a gas-and-dust flow or a slurry containing small particles, while said slurry is simultaneously superposed by ultrasonic oscillations and further agglomerated, the plastic deformation of a sintered billet intended to improve the homogeneity of its porous structure and the uniformity of properties, the generation of multi-layered porous structures

wherein each layer is made of powder having a different granulometric composition, the production of billets from the mixture of powders each having a different granulometric composition, forming a billet from the mixture of powders each having a different granulometric composition in a quasi-fluidized bed generated by an ascending gas flow, vibratory forming based on the segregation of powder particles or those of a pore-forming material according to pre-defined dimensions by means of superposing a mixture to be formed by a pre-defined amount of vibrations, chemical etching of a metal porous framework with simultaneously passing a pressurized gas through said framework, a mechanical or chemical addition of various pore-forming additives etc. [Belov S.V. Porous Metals in Machine Engineering. – M.:Machine Engineering, 1981. – p247.; Permeable Porous Materials: Reference Manual / under Edition of Belov S.V. – M.:Metallurgy, 1987. – p335.; Porous Powder Materials and Products thereof / Vityaz P.A., Kaptsevich V.M., Sheleg V.K.- Minsk.: Higher Education, 1987. – p164.; Structural Formation and Properties of Porous Powder Materials / Vityaz P.A., Kaptsevich V.M., Kostornov A.G. et al - M.:Metallurgy, 1993. – p240.; Vityaz P.A., Kaptsevich V.M., Sheleg V.K. Efficient Porous Powder materials and Deposition thereof in Machine Engineering. – Minsk: BelNIINTI, 1985. – p11.; Efficiency of Sintered Permeable Materials for Various Purposes / Vityaz P.A., Sheleg V.K., Kaptsevich V.M., Mazjuk V.V. // Collected Articles Powder Metallurgy. – Minsk: Higher Education, 1984. – Publication 8. – pp66-70.; Vityaz P.A., Kaptsevich V.M., Kusun R.A. Filtering Materials: Properties, Application Fields, Manufacturing Techniques. – Minsk.: NII PM with OP, 1999. – p304.].

The application of the above-described approaches and various combinations thereof substantially widens the possibilities of powder metallurgy when related to the variation of basic characteristics of porous powder products like: porosity from 30 to 70%, permeability factor from  $10^{-12}$  to  $10^{-9}\text{m}^2$ , maximum pore size up to 1000  $\mu\text{m}$ , average pore size from 0.1 to 500  $\mu\text{m}$ , specific surface from 0.01 to 1.0  $\text{m}^2/\text{g}$ , bending strength from 30 to 300 MPa, tensile strength from 20 to 480 MPa, heat conductivity factor from 0.1 to 150  $\text{W}/\text{m}\cdot\text{deg}$  etc.

Known are a number of methods of producing porous materials having an anisotropic porous structure, in particular, known is a method of producing multi-layer porous materials [USSR Author's Certificate No. 725820, B22F 7/02 Mishin I.A., Timopheev I.A. Method of Producing Sintered Multi-layer Products // published 05.04.80, Bulletin No. 13] comprising forming the packages of powders with different-sized particles wherein said particle size is decreased by 16 to 35  $\mu\text{m}$  in each of the subsequent layers, the compression of said layers in each package while decreasing the compression pressure of each layer by 300 MPa and further sintering. Known are methods of producing sintered multi-layer products, in particular heat pipe fuses, comprising a sequential compression of powder layers with the compression pressure of each subsequent layer being decreased by minimum 10 MPa and further sintering. [USSR Author's Certificate No. 1034273, Int. Cl.4 B22F 3/10. Method of Producing Sintered Porous Products from Titanium Powder// Maidanik U.F., Kuskov G.V., Gerasimov U.F. et al; USSR Author's Certificate No. 1491613, B22F 3/10 Kiseev V.M., Beljaev A.A., Zubarev A.Ju., Pogorelov N.P. // Method of Producing Sintered Multi-layer Products, Published 07.07.89, Bulletin No. 252].

The disadvantages of the methods known so far are as follows:

1. Complexity of the technique for producing multi-layered products;
2. Failure to produce large-length products due to probable misalignment during compression and sintering stages;

3. Complexity of bonding the above-described elements to porous and non-porous elements having different configurations and different chemical compositions;
4. Failure to produce materials having an anisotropic structure and a pore size ranging from  $\mu\text{m}$  to  $\text{nm}$ .

Known is a method of producing porous materials and a material produced according to this method (RU Patent No. 2175904, B22F3/10 Uvarov V.I., Borovinskaya I.P., Merzhanov A.G. Method of Producing Porous Materials and Material Produced thereby // published 20.11.03, Bulletin No.32) comprising the production of an exothermic powder mixture of primary elements in the ratio providing a self-sustained combustion of said mixture, the compression of said mixture in a mold having a pre-defined configuration, the thermal vacuum processing of a billet before its self-ignition with further sintering and subsequent cooling. The mixture formation is performed layer-by-layer from the powders of primary components having a similar or different composition, thickness and dispersion to provide a pore distribution factor from 69 to 95%.

The disadvantages of the above method are as follows:

1. Failure to produce products having an anisotropic structure and a pore size ranging from  $\mu\text{m}$  to  $\text{nm}$ .
2. Failure to produce large-length products due to probable misalignment of the products during a sintering stage;
3. Impossibility of bonding the above-described elements to porous and non-porous elements having different configurations and different chemical compositions due to high temperature of a sintering stage (up to  $3000^{\circ}\text{C}$ ).

Powder metallurgy approaches make it possible to produce porous materials with high mechanical strength, heat conductivity, liquid-and-gas permeability. However, a minimum size of powder particles used for producing permeable materials usually makes up of  $1\ \mu\text{m}$  which prevents the use of powder metallurgy approaches for producing materials with high specific surface and efficient pore size in a nanometric range like adsorbents and catalysts.

Scientific and technical tasks of producing adsorbents and catalysts i.e. porous materials with an efficient pore radius from 10 to 100 nm for specific surface up to several hundreds  $\text{m}^2/\text{g}$ , are solved by means of catalytic material science. The production of the above materials is based on colloid-chemistry approaches including the deposition of solid-phase ultra-disperse particles from the solutions of respective metal salts with further stages of rinsing, thickening, molding and baking [Structure and Properties of Adsorbents and Catalysts. Collection of Articles under Edition of Linsen B.G., M., Mir, 1973.- p 653; Production of Activated Alumina i.e. Carrier for Alumoplatinum Reforming Catalyst: Topical Surveys / TsNII of Informative and Technical-and-Economic Research in Petrol-refining and Petrol-chemical Industry; Compiled by Poyezd D.F., Radchenko E.D., Panchenkov G.M., Kolesnikov I.M. – M., 1973. – p 78; Dzisko V.A., Karnaukhov A.P., Tarasova D.V. Physical-and-chemical Basis of Oxide Catalyst Synthesis. Novosibirsk, Nauka, 1978. – p 384; Mukhlenov I.P., Dobkina E.I., Derjuzhkina V.I., Soroko V.E. Catalyst Technology.-L., Chemistry.- 1979.- p 328; Neymark I.E. Synthetic Mineral Adsorbents and Catalyst Carriers. Kiev: Navukova Dumke, 1982. - p 216; Keltsev N.V. Adsorption Technique Basis. - M., Chemistry, 1984.- p 592]. Porous permeable materials used as adsorbents and catalysts are presented nowadays by the two types of porous structures i.e. a globular type and a sponge type, though the materials with a globular structure find wider application (zeolites, silica gels, activated

alumina). The basic properties of a porous structure both for adsorbents and catalysts as well as for powder permeable materials are defined by the size and packaging approach of primary particles making a framework of a porous material.

The production of adsorbents and catalysts demands the application of various methods of adjusting (modifying) their structure to expand the versatility range of porous structures and considerably widen their application field. Modern methods of adjusting the properties of a porous structure during a deposition stage are mostly based on altering the supersaturation level and interfacial tension. The production of adsorbents exhibiting a relatively wide range of structural-adsorption properties (specific surface from 30 m<sup>2</sup>/g to 800 m<sup>2</sup>/g, pore volume up to 1.2 cm<sup>3</sup>/g) becomes possible due to varying the following factors: a solution pH and temperature, a precipitator type, an intermicelle liquid structure which is changed by adding the solution with electrolytes, surface-active and high-molecular substances, an ultrasonic treatment in electromagnetic fields, a co-deposition of hydrogels having different origin as well as various combinations thereof [ Ermolenko N.F., Efros M.D. Porous Structure Adjustment of Oxide Adsorbents and Catalysts.-Minsk, Nauka and Tekhnika .-1971.-p 280; Neymark I.E. Directional Synthesis and Means to Adjust Porous Structure and Adsorbent Properties. – From the Book Adsorbents, Production, Properties, Application. – L.: Nauka, 1971, pp 5-12; Komarov V.S. Adsorbents and their Properties. – Minsk: Nauka and Tekhnika . – 1977. – p 248; Komarov V.S., Dubnitskaya I.B. Physical-and-chemical Basis of Porous Structure Adjustment for Adsorbents and Catalysts. – Minsk, Nauka and Tekhnika, 1988, p 288].

A hydro-thermal method considered as the most efficient method of modifying a porous structure at a xerogel formation stage [Barrer P. Hydro-thermal Chemistry of Zeolites. M., Mir., 1985.- p 424; Kiselev A.V., Nikitin Ju.S., Oganessian E.B. Time Influence of Hydro-thermal Treatment on Variations of Industrial Silicagel Pore Structure and Skeleton // Collective Journal – 1969. –T31.- pp 525-531; Research of Super-porosity Formation in Silicagel during Hydro-thermal Treatment / Gorelik P.L., Zhuravlev L.T., Kiselev A.V. et al // Collective Journal – 1971. – Vol. 33. – pp 51-58; Influence of Primary Silica Structure on Nature of Super-porosity of Modified Samples Produced by Hydro-thermal Treatment / Gorelik R.L., Davidov V.Ja., Zhuravlev L.T. et al // Collective Journal – 1973. – Vol. 35. – pp 456-461; Buman R.K., Mironovich A.A. Influence of Oproduction and Desorption Properties of Boehmite on Aggregate Properties of Water Media and Temperature during Hydro-thermal Treatment of Hydrargillite // ; Chertov V.M., Neymark I.E. Research of Silicagel Hydro-thermal Ageing in Various Salt Solutions // Colloid Journal-1967.-Vol. 29, No. 2 -pp 299-302; Influence of Hydro-thermal Treatment Temperature on Changes in Pore Structure and Skeleton of Model Silicagel /Kiselev A.V, Lukjaniovich V.M., Nikitin Ju.S. et al//Colloid Journal.-1969.-Vol.31,No.3-pp 385-393; Chertov V.M., Zelentsov V.I. Effect of Hydrothermally Modified Alumohydrogel on Xerogel Texture//Ukraine Chemical journal.-1972.-Vol.38, No.10.-pp 996-1001; Karnaukhov A.P. Geomettry of Catalysts// Cynetics and Catalysts-1982.-Vol.23 No. 6 -pp 1438-1448] is based on the interaction between a porous body and water (aqueous solutions) in a closed autoclave space and makes it possible to provide a porous structure adjustment in wider ranges than during a deposition stage. The flexibility of a hydro-thermal method is provided in a large extent by high solubility of water which is increased with the temperature rise due to the destruction of hydrogen contacts and numerous growth of water monomer molecules (40% at 100°C and 80% at 250°C) [ Erdei-Grouz T. Transfer Activities in Aqueous Solutions.-M.:Mir, 1976.-p 595; Bozhenov P.I. Technique of

Autoclave Materials.-L.: Stroyizdat, 1978.-p 368]. A hydro-thermal treatment of adsorbents results in a sharp decrease of their specific surface and in an increase of a pore size with the total pore volume remaining substantially constant which can be explained by the dissolution of small particles, the diffusion transfer of a solute and its deposition onto larger-sized particles and onto negative curvature surfaces in the areas of inter-particle contacts. Hence, a hydro-thermal modification in general terms presents a diffusion coagulation process i.e. "eating" smaller particles by larger ones. Like all the spontaneous processes those occurring during a hydro-thermal modification, e.g. sintering, crystallization from the solution or from the melt flow etc. are caused by the decrease of a system free energy and result in the cutting down of interfacial surfaces. A hydro-thermal modification makes it possible to adjust an adsorbent porous structure in wider ranges. This method is used to produce, for example silikagels both micro-pore and macro-pore ones having the pore volume from 0.3 to 2.5 cm<sup>3</sup>/g, the specific surface from 1 to 800m<sup>2</sup>/g and the pore diameter from 2 to 1000 nm. However, industrial oxide adsorbents and catalysts have a low heat conductivity of max. 0.2 W/(mK) and their mechanical strength as a rule is within the range from 10 to 15 MPa since a high-temperature sintering stage has been eliminated due to possible crucial changes of a material pore structure. None of the methods of a material porous structure adjustment known so far makes it possible to produce a material with through-pores sized from 5 to 50 μm and moreover to provide high gas-and-fluid permeability. Besides, the most important problem of catalyst material science still an unsolved one is the production of porous products having complex configurations and various dimensions including those capable of bonding to porous and non-porous elements of metal and ceramic structures.

Eventually, despite a substantial progress in the field of producing porous non-organic materials the demand in new useful types of porous materials calls for the development of advanced synthesis methods which would make it possible to produce the materials having the pores sized both in a nano-and-micrometer range and providing the possibility of simultaneously conducting the processes of adsorption, diffusion, viscous gas-and-fluid flow and of adjusting the porous body formation processes.

In this connection the production of porous ceramics on the base of aluminum hydroxide and alumina by a hydro-thermal treatment of metallic aluminum in a high-disperse or foil state becomes widely used for synthesis of porous materials i.e. carriers and catalysts despite its relatively high energy consumption for the production of primary materials (high-temperature electrolysis, dispersion during powder production, rolling during foil production etc.) (I.Sungkono, H.Kameyama, T.Koya "Development of Catalytic Combustion Technology of VOC Materials by Anodic Oxidation Catalysts", Appl.Surf.Sci., 1997, V. 121/122, p. 424-438; G.Pataerमारakis, N.Nicopoulos "Catalysis over Porous Anodic Film Catalysts with Different Pore Surface Concentration", J.Catal., 199, V.187, p.311-320; N.Burgos, M.Paulis, M.M.Antxustegi, M.Montes "Deep Oxidation of VOC Mixtures with Platinum Supported on Al<sub>2</sub>O<sub>3</sub>/Al Monoliths", Appl.Catal.B, 2002, V.38, p. 251-258, Ananjin V.N., Belyaev V.V., Parmon V.N., Sadykov V.A., Tikhov S.F., Starostina T.G. "New Materials Based on Aluminum Compositions for Solving Ecological Problems and Non-traditional Energy Problems", Report Thesis of XIV Mendeleev Congress on General and Applied Chemistry (Belarus, Minsk, 1993), Minsk: "Navuka and Tekhnika", 1993, Vol.1, pp 35-36; Jakerson V.I., Dyikh Zh.P., Subbotin A.N., Gudkov B.S., Chertkova S.V., Radin A.N., Boevskaya E.A., Chertichnik Z.A., Golosman E.Z., Samurzina R.G. "Catalysts Produced on the Base of Activated Aluminum Alloys///. Production of Alumooxide Catalysts."//Cinetics and Catalysis – 1995.- Vol.

356. Publication 6, pp 918-933) of Sensor Devices (Varghese O.K., Gong D., Paulose M., Ong K.G., Crimes C.A., Dickey E.C. "Highly Ordered Nonporous Alumina Films: Effect of Pore Size and Uniformity on Sensing Performance" (J.Mater.Res., 2002, Vol. 17, No.5, pp 1162-1171), of filtering elements (Solntsev K.A., Shustorovich E.M., Chernjavsky A.C., Dudenkov I.V. "Oxidative Designing of Thin-Wall Ceramics above Metal Melting Temperature": Production of Oxide Fibers from Aluminum and its Alloys", RAN Report, 2002, Vol. 385, No.3, pp 372-377). This method of porous material synthesis makes it possible to produce alumina with advanced texture, mechanical and chemical properties that are impossible to achieve with alumina synthesized on the base of primary solutions of aluminum salts by means of crystallization (deposition) from the solution.

The technique of producing the above materials is based on combining the colloid chemistry approaches and those of powder metallurgy as well as on the ability of aluminum powder to provide a hydrolytic chemical reaction under hydrothermal conditions with the formation of a porous composite  $\text{Al}_2\text{O}_3/\text{Al}$  or  $\text{Al}(\text{OH})_3/\text{Al}$ . New ceramic materials as to their porous structure and mechanical properties occupy an intermediate position between well-known granulated ceramic materials produced by colloid chemistry approaches and powder permeable materials produced by powder metallurgy approaches. A hydrothermal synthesis (HTS) of porous ceramics opens wide perspectives for the development of porous materials having a wide application field. When used for powder-like components having different composition, chemical origin and differently responding to a hydrolytic reaction the above-described method provides for the production of materials with a unique combination of properties which is impossible to achieve by conventional approaches of colloid chemistry and powder metallurgy.

First information about the aggregation of aluminum powder during long storage time (from several months to a year) under humid conditions was published in mid seventies (Rojkh I.L., Litovchenko N.A., Belitskaya S.G. et al Research of Disperse Aluminum Oxidation Process // Powder Metallurgy.-1976.-No.1.-pp 56 to 59). The authors of the above-mentioned article give the following description of the aggregation mechanism. Packaging of aluminum particles in a powder layer generates favorable conditions for the sorption and capillary condensation of water vapors. A chemical reaction of powder with water in the area of inter-particle contacts results in the hydration of an oxide film covering aluminum particles. The hydration products produce a new pore system which promotes the adsorption, speeds up the hydration and improves the permeability of an oxide film (all this accompanied by a sharp increase of specific surface). The increase of an oxide film layer thickness causes the aggregation of particles and the slowdown of the reaction. High dispersion of aluminum powders multiplies their hydration ability, and this in its turn claims more rigid requirements to the storage conditions of aluminum powders.

Known are a number of inventions, wherein the chemical activity of disperse aluminum is used for conducting hydro-thermal synthesis for producing a porous composite  $\text{Al}_2\text{O}_3/\text{Al}$  or  $\text{Al}(\text{OH})_3/\text{Al}$  having high specific surface, high mechanical strength and a system of through-pores sized up to 10  $\mu\text{m}$ .

The nearest Prior Art references to the engineering solutions filed are the following:

Method of Producing Porous Ceramic Material (Author's Certificate 1600930 Method of Producing Porous Ceramic Material // Azarov C.M., Romanenkov V.E., Grishin S.I., Smirnova T.A., Smirnov V.G. //SU patent application No.4469913/31-02, filed 29.07.1988, published 23.10.1990, Bull. 39//Discoveries Inventions.-1990-No.38-p 84) comprising the injection of aluminum powder into a mold followed by

several treatment cycles, wherein each treatment cycle includes a water vapor treatment and a subsequent thermal treatment in the air at the temperature from 140 to 170°C for 3-5 hrs and at the temperature from 620 to 660°C with the aim of increasing the strength of ceramic products.

Method of Catalyst Production (RU Patent 2131774 BO1J 37/02 Tikhov S.F., Sadykiv V.A., Kruglyakov V.Ju., Pavlova S.N. et al Method of Catalyst Production for Deep Oxidation of Hydrocarbons and Carbon Monoxide// published 20.06.1999) comprising the formation of the mixture of insoluble or poorly soluble compounds with powder-like aluminum, the injection of said mixture into a mold and the treatment by water vapors with further baking.

Method of Porous Membrane Production (USSR Author's Certificate 15611999, Int.Cl. Method of Porous Membrane Production //Azarov S.M., Gorobtsov V.G., Grishin S.I., Litvinets M.A., USSR). – No. 4469413/31-26, filed 29.07.1988, Published 07.05.1990, Bull. No.17 // Discoveries Inventions. – 1990 – No. 17 – p 97), comprising the deposition of ceramics or a metal from a water slurry containing the mixture of aluminum powder with ceramic powder onto the surface of a porous carrier (substrate), partial filling of the substrate porous tunnels, pre-treatment in water vapor media at the temperature from 140 to 170°C and a final thermal treatment at the temperature from 400 to 600°C with the aim of increasing the uniformity of a membrane porous structure and improving the mechanical bonding strength between a porous layer and a carrier.

It is common for all of the foregoing inventions that synthesis is conducted in an autoclave in water vapor media at exceedingly high pressures and temperatures of 250°C which results in a number of disadvantages. Firstly, the necessity of using an autoclave substantially decreases the technical possibilities of synthesis due to dimensional limitations of the products. Secondly, a treatment by water vapors of disperse aluminum loaded into a mold involves certain difficulties caused by the necessity to force out the air from the powder porous space to provide the required contact of aluminum with water vapors. Besides, the properties of the material synthesized in an autoclave are substantially decreased.

The increase of the water temperature improves its dissolving capacity, however, the ultimate concentration of poorly soluble substances is actually unchanged at variations of the solution temperature. Hence, during synthesis of a porous composite  $\text{Al}(\text{OH})_3/\text{Al}$  the supersaturation of the solution is to be provided by vaporizing the solvent i.e. water. However, synthesis of a porous composite in an autoclave in water vapor media proceeds in a closed and constant space of water vapors and at the constant temperature. These conditions essentially do not provide any possibility of controlling the supersaturation procedure. Besides, the solubility of aluminum hydroxide is increased with the temperature increase and as a result the supersaturation is decreased with the resulting formation of large boehmite crystallites up to 1 to 2  $\mu\text{m}$ . Hence, this explains a low mechanical strength of a composite at 250°C in an autoclave and the decrease of its specific surface.

Thus, there is an essential demand in a new method of disperse aluminum treatment which would make it possible to control the crystallization process, to prevent diffusion limitations, to produce composite porous materials with pre-defined properties and to substantially expand the technical possibilities of the method.



## SUMMARY OF THE INVENTION

It is the aim of the present invention to create advanced porous composite materials having an anisotropic porous structure and the new methods of their synthesis from inexpensive primary materials.

It is a further aim of the present invention to facilitate the use of inexpensive primary materials and to do away with power-consuming and expensive hydrothermal synthesis making it possible to conduct the synthesis procedure at the maximum temperature of 100°C.

Further the present invention provides for the production of a supersaturated solution by means of vaporizing a solvent fraction during synthesis.

Further the present invention provides for the production of a porous composite both in a mold and on the surface of a solid substrate in the form of a layer having a pre-defined thickness.

Finally the present invention makes it possible to control the aluminum transformation level and thus to adjust the mechanical and structural properties of a synthesized material which none of the existing methods is capable of.

The foregoing aims in the first embodiment of a synthetic composite material in the form of a solid with a porous-open structure of crystallite aggregates of aluminum hydroxide ( $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$ ) or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) coupled by phase contacts are achieved due to said material made with the specific surface from 50 to 200  $\text{m}^2/\text{g}$ , while the space between said crystallites presents pores having a diameter from 4.5 nm to 100  $\mu\text{m}$  and said material is synthesized by the dissolution of disperse aluminum in an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  at the maximum temperature of 100°C (preferably from 85 to 95°C) followed by the mass crystallization of aluminum hydroxide from a supersaturated solution of aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts.

The material could additionally comprise separate aluminum particles surrounded by porous shells composed of crystallite aggregates of aluminum hydroxide ( $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$ ) or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) and coupled by phase contacts.

The size of resulting crystallites preferably makes up from 200 to 1000 nm (Fig. 1b, Fig.5).

The material could be synthesized from disperse aluminum pre-formed by any arbitrary means or from a powder-like material coated by an aluminum layer, while the dissolution of aluminum during the material synthesis is provided in the process of a heterogeneous chemical reaction of aluminum with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$ , preferably by means of impregnating a pre-formed powder with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  in the volume of 0.01 to 0.95 of the pore volume of powder media, preferably at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

An additional dissolution of aluminum during the material synthesis could be provided by means of impregnating a cooled pre-formed porous body with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  in the volume equal to the material pore volume, preferably followed by the thermal treatment at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

The material is preferably characterized by an adsorption-desorption isotherm shown in Fig.3, graph 1 and a pore size distribution shown in Fig. 4, graph 1.

The material could be additionally subjected to a thermal treatment at the temperature from 450<sup>0</sup> to 550<sup>0</sup>C until aluminum hydroxide is fully transformed into alumina.

The material is preferably characterized by a microstructure shown in TEM micrograph (Fig. 6) and an adsorption-desorption isotherm shown in Fig. 3, graph 2.

The above-described procedures could be performed a number of cycles during the material synthesis.

The material is preferably characterized by the structural dependence on the aluminum transformation level shown in SEM micrograph Fig. 10. The specific features for the aluminum transformation level of 0.5 are as follows: an adsorption-desorption isotherm shown in Fig. 9, graph 1, the dependence of the aluminum-to-alumina transformation level on the number of cycles shown in Fig. 7, the dependence of the specific surface and the sorption pore volume on the number of cycles shown in Fig. 8 and the dependence of the mechanical strength on the number of cycles shown in Fig. 11.

The foregoing aims in the second embodiment of a synthetic composite material in the form of a solid with a porous-open structure of crystallite aggregates of aluminum hydroxide ( $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$ ) or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) coupled by phase contacts are achieved due to said material made with the specific surface from 50 to 450  $\text{m}^2/\text{g}$  and comprising metallic organic and/or inorganic, non-porous and porous disperse particles of various configurations and/or continuous fibers (threads) coupled by mechanical and/or phase contacts in the form of crystallite aggregates of aluminum hydroxide ( $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$ ) or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ), while the space between said crystallites and disperse particles presents pores having a diameter from 4.5 nm to 360  $\mu\text{m}$  and said material is synthesized by the dissolution of disperse aluminum in an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  at the maximum temperature of 100<sup>0</sup>C (preferably from 85 to 95<sup>0</sup>C) followed by the mass crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts.

The material could additionally comprise separate aluminum particles surrounded by porous shells composed of crystallite aggregates of aluminum hydroxide ( $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$ ) or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) and coupled by phase contacts in the form of crystallite aggregates having a similar structure.

The material could be synthesized from a mixture pre-formed by any arbitrary means and comprising metallic organic and/or inorganic, non-porous and porous disperse particles of various configurations and/or continuous fibers (threads) and disperse aluminum or other disperse material coated by an aluminum layer, while the dissolution of aluminum during the material synthesis is provided in the process of a heterogeneous chemical reaction of aluminum with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$ , preferably by impregnating a pre-formed porous body with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$ , in the volume of 0.01 to 0.95 of the total pore volume of powder media, preferably at the temperature from 85 to 95<sup>0</sup>C for 1.5-2 hrs until water is fully vaporized.

An additional dissolution of aluminum during the material synthesis could be performed in the process of a heterogeneous chemical reaction of aluminum with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$ , preferably by means of impregnating a pre-formed porous body with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  in the volume of 0.01 to 0.95 of the pore volume of powder media, preferably at the temperature from 85 to 95<sup>0</sup>C for 1.5-2 hrs until water is fully vaporized.

The material could be additionally subjected to a thermal treatment at the temperature from 450<sup>0</sup> to 550<sup>0</sup>C until aluminum hydroxide is fully transformed into alumina.

The above-described procedures could be performed a number of cycles during the material synthesis.

The material could be made from the mixture of aluminum powder with zeolite and activated alumina and be characterized by the following specific features: the structure shown in SEM micrograph (Fig. 12), the adsorption-desorption isotherms shown in Fig. 14, 16, 17, the dependence of the sorption pore volume of composite NaA/Al/Al(OH) on the ratio of zeolite powder/aluminum powder shown in Fig.15, the dependence of the mechanical strength on the dispersion and the content of adsorbent shown in Fig. 18.

The material is preferably characterized by the dependence of the mechanical strength on the aluminum transformation level (number of treatment cycles) for various powder-like adsorbents shown in Fig. 19.

The foregoing aims in the third embodiment of a synthetic composite material in the form of a solid with a porous-open structure of crystallite aggregates of aluminum hydroxide (Al(OH)<sub>3</sub> or AlOOH) or alumina (γ-Al<sub>2</sub>O<sub>3</sub>) coupled by phase contacts are achieved due to said material made with the specific surface from 50 to 200 m<sup>2</sup>/g and presenting a layer having a thickness from 3 to 50 of the particle diameters of primary aluminum powder deposited on the whole or a fraction of a solid substrate surface of aluminum or any other metal or nonmetal coated by an aluminum layer and coupled to said substrate by crystallite aggregates of (Al(OH)<sub>3</sub> or AlOOH) hydroxide or alumina (γ-Al<sub>2</sub>O<sub>3</sub>), while the space between said crystallites presents pores having a diameter from 4.5 nm to 100 μm and said material is synthesized by the dissolution of aluminum in an aqueous solution having pH=7.5-11.5 at the maximum temperature of 100<sup>0</sup>C (preferably from 85 to 95<sup>0</sup>C) followed by the mass crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving disperse and solid aluminum.

The material could additionally comprise separate aluminum particles surrounded by porous shells composed of crystallite aggregates of aluminum hydroxide (Al(OH)<sub>3</sub> or AlOOH) or alumina (γ-Al<sub>2</sub>O<sub>3</sub>) and coupled by phase contacts in the form of crystallite aggregates having a similar structure, while a disperse aluminum layer could be deposited onto the surface of said substrate by dipping, spraying or spreading, for example, from a volatile liquid slurry containing aluminum particles, and the dissolution of aluminum during the material synthesis is provided in the process of a heterogeneous chemical reaction of aluminum with an aqueous solution having pH=7.5-11.5, preferably by impregnating a pre-formed porous body with an aqueous solution having pH=7.5-11.5, in the volume of 0.01 to 0.95 of the pore volume of powder media, preferably at the maximum temperature of 100<sup>0</sup>C for 2-3 hrs.

The material could be additionally subjected to a thermal treatment at the temperature from 450<sup>0</sup> to 550<sup>0</sup>C until aluminum hydroxide is fully transformed into alumina and, when used as a layer on a solid aluminum substrate, it is characterized by a structure shown in SEM micrograph in Fig. 20 and also by adsorption-desorption isotherms shown in Fig. 21.

The foregoing aims in the forth embodiment of a synthetic composite material in the form of a solid with a porous-open structure of crystallite aggregates of aluminum hydroxide (Al(OH)<sub>3</sub> or AlOOH) or alumina (γ-Al<sub>2</sub>O<sub>3</sub>) coupled by phase contacts are achieved due to said material made with the specific surface from 50 to 200 m<sup>2</sup>/g and on the surface of one or a number of porous or non-porous, nonmetallic or metallic elements coupled by mechanical or phase contacts in the form of crystallite aggregates of (Al(OH)<sub>3</sub> or

AlOOH) hydroxide or alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), while the space between said crystallites presents pores having a diameter from 4.5 nm to 100  $\mu$ m and said material is synthesized by the dissolution of disperse aluminum in an aqueous solution having pH=7.5-11.5 at the maximum temperature of 100°C (preferably from 85 to 95°C) followed by the mass crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum and in the area of inter-particle contacts.

The material could additionally comprise separate aluminum particles surrounded by porous shells composed of crystallite aggregates of aluminum hydroxide (Al(OH)<sub>3</sub> or AlOOH) or alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and coupled by phase contacts in the form of crystallite aggregates having a similar structure.

A disperse aluminum layer during the material synthesis could be deposited on the whole or a fraction of the surface of a porous or non-porous, nonmetallic or metallic element, for example, in the shape of a pipe, sheet or a bush by dipping, spraying or spreading, for example, from a volatile liquid slurry containing aluminum particles, while the dissolution of aluminum during the material synthesis is provided in the process of a heterogeneous chemical reaction of aluminum with an aqueous solution having pH=7.5-11.5, preferably by impregnating a pre-formed porous body with an aqueous solution having pH=7.5-11.5, in the volume of 0.01 to 0.95 of the pore volume of powder media, preferably at the maximum temperature of 100°C for 2-3 hrs.

An additional dissolution of aluminum could be performed in the process of a heterogeneous chemical reaction of aluminum with an aqueous solution having pH=7.5-11.5, preferably by means of impregnating a pre-formed porous body with an aqueous solution having pH=7.5-11.5 in the volume equal to the pore volume of powder media, preferably at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

The material could be additionally subjected to a thermal treatment at the temperature from 450° to 550°C until aluminum hydroxide is fully transformed into alumina.

The above-described procedures could be performed a number of cycles during the material synthesis.

During the material synthesis the porous or non-porous, nonmetallic or metallic elements with a pre-deposited porous layer could be placed into a divided or a solid mold in the required succession with further filling-in the spaces between said elements and between said elements and said mold with disperse aluminum or other disperse material coated by an aluminum layer or by a slurry of disperse aluminum or other disperse material coated by an aluminum layer, while the dissolution of aluminum during the material synthesis is provided in the process of a heterogeneous chemical reaction of aluminum with an aqueous solution having pH=7.5-11.5, preferably by impregnating the pre-formed elements with an aqueous solution having pH=7.5-11.5, in the volume of 0.01 to 0.95 of the pore volume of powder media, preferably at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

An additional dissolution of aluminum could be provided in the process of a heterogeneous chemical reaction of aluminum with an aqueous solution having pH=7.5-11.5, preferably by means of impregnating a pre-formed porous body with an aqueous solution having pH=7.5-11.5 in the volume equal to the pore volume of powder media, preferably at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

The material could be additionally subjected to a thermal treatment at the temperature from 450<sup>0</sup> to 550<sup>0</sup>C until aluminum hydroxide is fully transformed into alumina.

The above-described procedures could be performed a number of cycles during the material synthesis.

The foregoing aims in the fifth embodiment of a synthetic composite material in the form of a solid with a porous-open structure of alumina aggregates coupled by phase contacts are achieved due to said material made with the specific surface up to 20 m<sup>2</sup>/g and presenting a system of filament nanocrystals of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and a system of hollow spheres of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> coupled by phase contacts in the form of sintered crystallite aggregates of alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>), while the space between said crystallites presents pores having a diameter from 4.5 nm to 100  $\mu$ m and said material is synthesized by the dissolution of aluminum in an aqueous solution having pH=7.5-11.5 at the maximum temperature of 100<sup>0</sup>C (preferably from 85 to 95<sup>0</sup>C) followed by the mass crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts and subsequent baking at the temperature from 750 to 1450<sup>0</sup>C until aluminum hydroxide is fully transformed into corundum.

The material could be preferably synthesized from disperse aluminum or continuous/discontinuous aluminum fibers (wires) pre-formed by any arbitrary means, while the dissolution of aluminum during the material synthesis is provided in the process of a heterogeneous chemical reaction of aluminum with an aqueous solution having pH=7.5-11.5, preferably by impregnating a pre-formed porous body with an aqueous solution having pH=7.5-11.5 in the volume of 0.01 to 0.95 of the pore volume of powder media, preferably at the temperature from 85 to 95<sup>0</sup>C for 1.5-2 hrs until water is fully vaporized.

The above-described procedures could be performed a number of cycles during the material synthesis.

It is preferable during the material synthesis to perform an additional thermal treatment of a porous material at the temperature from 750 to 1450<sup>0</sup>C until aluminum is fully vaporized and aluminum hydroxide and aluminum are fully transformed into corund (alumina  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>), while the material is preferably characterized by the following: a microstructure shown in SEM micrograph (Fig. 26, 27), the dependence of adsorption-desorption isotherms on the baking temperature, shown in Fig. 28, a and the dependence of the specific surface and the sorption pore volume on the baking temperature shown in Fig. 28, b.

The foregoing aims in the first embodiment of a method of producing a synthetic composite material including the formation of disperse aluminum or other disperse material coated by an aluminum layer, the dissolution of aluminum and the crystallization of aluminum hydroxide are achieved due to said aluminum being dissolved by means of impregnating the pre-formed layer with an aqueous solution having pH=7.5-11.5 in the volume of 0.01 to 0.95 of the total pore volume, while the subsequent mass crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts is provided by keeping in the air at the maximum temperature of 100<sup>0</sup>C (preferably from 85 to 95<sup>0</sup>C) for 1.5-2 hrs until water is fully vaporized.

It is preferable to provide an additional dissolution of aluminum by means of the thermal treatment of a cooled pre-formed porous body which has been impregnated with an aqueous solution having pH=7.5-11.5 in the volume equal to the pore volume of the material at the temperature from 85 to 95<sup>0</sup>C for 1.5-2 hrs until water is fully vaporized.

The material could be additionally subjected to a thermal treatment at the temperature from 450° to 550°C until aluminum hydroxide is fully transformed into alumina.

The above-described procedures could be performed a number of cycles.

The foregoing aims in the second embodiment of a method of producing a synthetic composite material including mixing the insoluble or slow soluble compounds in the form of metallic, organic and/or inorganic, non-porous and porous disperse particles of various configurations and/or continuous fibers (threads) and disperse aluminum or other disperse material coated by an aluminum layer, the formation of said mixture, the dissolution of aluminum and the subsequent crystallization of aluminum hydroxide are achieved due to the dissolution of aluminum being performed by means of impregnating a pre-formed powder mixture with an aqueous solution having pH=7.5-11.5 in the volume of 0.01 to 0.95 of the total pore volume, while the subsequent mass crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts is provided by keeping in the air at the maximum temperature of 100°C (preferably from 85 to 95°C) for 1.5-2 hrs until water is fully vaporized.

An additional dissolution of aluminum is preferably performed by means of impregnating a cooled pre-formed porous body with an aqueous solution having pH=7.5-11.5 in the volume equal to the pore volume of the material and a subsequent thermal treatment of said porous body at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

The material could be additionally subjected to a thermal treatment at the temperature from 450° to 550°C until aluminum hydroxide is fully transformed into alumina.

The above-described procedures could be performed a number of cycles.

The foregoing aims in the third embodiment of a method of producing a synthetic composite material including the preparation of a slurry of disperse aluminum or other disperse material coated by an aluminum layer in a carrier, preferably a volatile one, the deposition of said slurry on a fraction or on the whole surface of a solid substrate made of aluminum or any other material coated by aluminum, drying of said layer, the dissolution of aluminum and the subsequent crystallization of aluminum hydroxide are achieved due to the dissolution of aluminum performed by impregnating a coated layer with an aqueous solution having pH=7.5-11.5 in the volume of 0.01 to 0.95 of the total pore volume, while the subsequent crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts is provided by keeping in the air at the maximum temperature of 100°C (preferably from 85 to 95°C) for 1.5-2 hrs until water is fully vaporized.

The deposition of a disperse aluminum layer onto the surface of a solid substrate is preferably provided by means of dipping, spraying or spreading.

An additional deposition of a disperse aluminum layer could be performed once or a number of times to provide the required thickness of a final layer. After depositing each layer the dissolution of aluminum is performed by means of impregnating a pre-deposited layer with an aqueous solution having pH=7.5-11.5 in the volume of 0.01 to 0.95 of the total pore volume, while the subsequent crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of

dissolving aluminum particles and in the area of inter-particle contacts is provided by keeping in the air at the maximum temperature of 100°C (preferably from 85 to 95°C) for 1.5-2 hrs until water is fully vaporized.

The material could be additionally subjected to a thermal treatment at the temperature from 450° to 550°C until aluminum hydroxide is fully transformed into alumina.

The foregoing aims in the forth embodiment of a method of producing a synthetic composite material including the deposition of a disperse aluminum layer or other disperse material coated by an aluminum layer onto the surface of one or a number of porous or nonporous, nonmetallic or metallic elements are achieved due to the dissolution of aluminum performed by means of impregnating a pre-deposited layer with an aqueous solution having pH=7.5-11.5 in the volume of 0.01 to 0.95 of the total pore volume, while the subsequent crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts is provided by keeping in the air at the maximum temperature of 100°C (preferably from 85 to 95°C) for 1.5-2 hrs until water is fully vaporized.

The deposition of a disperse aluminum layer onto the surface of one or a number of porous or nonporous, nonmetallic or metallic elements is preferably provided by means of dipping, spraying or spreading.

An additional dissolution of aluminum is preferably performed by means of impregnating a cooled pre-formed porous body with an aqueous solution having pH=7.5-11.5 in the volume equal to the pore volume of the material and by the subsequent thermal treatment of said porous body at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

The material could be additionally subjected to a thermal treatment at the temperature from 450° to 550°C until aluminum hydroxide is fully transformed into alumina.

The above-described procedures could be performed a number of cycles.

During the material synthesis the porous or non-porous, nonmetallic or metallic elements with a porous layer deposited thereon could be placed in the required succession into a divided or a solid mold with further filling-in the spaces between said elements and between said elements and said mold with disperse aluminum or other disperse material coated by an aluminum layer or by a slurry of disperse aluminum or other disperse material coated by an aluminum layer, while the dissolution of aluminum during the material synthesis is performed preferably by impregnating the pre-formed elements with an aqueous solution having pH=7.5-11.5 in the volume of 0.01 to 0.95 of the pore volume of powder media, preferably at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

An additional dissolution of aluminum is preferably performed by means of impregnating a cooled pre-formed porous body with an aqueous solution having pH=7.5-11.5 in the volume equal to the pore volume of the material and a subsequent thermal treatment of said porous body at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

The material could be additionally subjected to a thermal treatment at the temperature from 450° to 550°C until aluminum hydroxide is fully transformed into alumina.

The above-described procedures could be performed a number of cycles.

The foregoing aims in the fifth embodiment of a method of producing a synthetic composite material including the formation of aluminum powder, the dissolution of aluminum and the subsequent crystallization of aluminum hydroxide are achieved due to the dissolution of aluminum performed by means of impregnating a pre-formed powder with an aqueous solution having  $\text{pH}=7.5\text{--}11.5$  in the volume of 0.01 to 0.95 of the pore volume of powder media, while the subsequent crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts is provided by keeping in the air at the maximum temperature of  $100^{\circ}\text{C}$  (preferably from  $85$  to  $95^{\circ}\text{C}$ ) for 1.5-2 hrs until water is fully vaporized followed by baking at the temperature from  $750$  to  $1450^{\circ}\text{C}$  to vaporize aluminum until aluminum hydroxide is fully transformed into corundum.

An additional dissolution of aluminum is performed by means of the thermal treatment of a cooled pre-formed porous body with an aqueous solution having  $\text{pH}=7.5\text{--}11.5$  in the volume equal to the pore volume of the material at the temperature from  $85$  to  $95^{\circ}\text{C}$  for 1.5-2 hrs until water is fully vaporized.

The material could be additionally subjected to a thermal treatment at the temperature from  $450^{\circ}$  to  $550^{\circ}\text{C}$  until aluminum hydroxide is fully transformed into alumina.

The above-described procedures could be performed a number of cycles.

The material is additionally subjected to one more thermal treatment at the temperature from  $750$  to  $1450^{\circ}\text{C}$  to vaporize aluminum until aluminum hydroxide is fully transformed into corundum ( $\alpha\text{-Al}_2\text{O}_3$ ).

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates a SEM micrograph of a fracture of a porous composite  $\text{Al}/\text{Al}(\text{OH})_3$ , example 1.

Fig. 2 illustrates a size distribution histogram of macropores.

Fig. 3, graph 1 illustrates an adsorption-desorption isotherm of benzene on a porous composite  $\text{Al}/\text{Al}(\text{OH})_3$ , graph 2 illustrates an adsorption-desorption isotherm of benzene on a porous composite  $\text{Al}/\text{Al}_2\text{O}_3$ .

Fig. 4 illustrates a pore size distribution: graph 1 corresponds to a porous composite  $\text{Al}/\text{Al}_2\text{O}_3$  for the aluminum transformation level of 0.15, graph 2 corresponds to a porous composite  $\text{Al}/\text{Al}_2\text{O}_3$  for the aluminum transformation level of 0.5.

Fig. 5a, b illustrates a microstructure and an electron-diffraction pattern of a porous aggregate composed of aluminum hydroxide crystallites ( $\text{Al}(\text{OH})_3$ ) on the surface of aluminum particles and in the contact areas.

Fig. 6 illustrates a microstructure and an electron-diffraction pattern of activated  $\text{Al}_2\text{O}_3$  produced by a thermal decomposition of aluminum hydroxide at  $550^{\circ}\text{C}$ .

Fig. 7 illustrates the dependence of the aluminum transformation level on the number of cycles.

Fig. 8 illustrates the dependence of the specific surface and sorption pore volume values on the aluminum transformation level.

Fig. 9 illustrates the benzene adsorption isotherm on a porous composite  $\text{Al}/\text{Al}_2\text{O}_3$  for aluminum transformation levels of 0.5(1) and 0.15(2).

Fig. 10 illustrates a SEM micrograph of synthesized composite ceramics presenting different stages of a microstructure formation dependent on the aluminum transformation level.

Fig. 11 illustrates the dependence of the mechanical compression strength of a porous composite  $\text{Al}/\text{Al}_2\text{O}_3$  on the aluminum transformation level.



Fig. 12 illustrates a microstructure of composite ceramics of zeolite NaX/Al/Al(OH)<sub>3</sub> (a) and activated alumina /Al/Al(OH)<sub>3</sub> (b).

Fig. 13 illustrates the size distribution histograms of supermacropores in porous composites on the base of powder-like activated alumina A-1 (graph a) and zeolite NaX (graph b).

Fig. 14 illustrates the adsorption-desorption isotherms of benzene-and-water vapors on a porous composite of zeolite NaA/Al/Al(OH)<sub>3</sub> with various sizes of powder-like zeolite particles and the mass ratio of powder-like components 2:1.

Fig. 15 illustrates the dependence of the pore sorption volume value on the mass fraction of aluminum powder in the mixture.

Fig. 16 a, b illustrates an adsorption isotherm of benzene-and-water vapors on a porous composite of NaY/Al/Al(OH)<sub>3</sub>.

Fig. 17 illustrates the adsorption-desorption isotherms of benzene-and-water vapors on a porous composite of activated alumina A-1/Al/Al(OH)<sub>3</sub>.

Fig. 18 illustrates the isolines of the mechanical compression strength for porous composites in  $r - \omega$  coordinates, where  $r$  is a particle size of powder-like industrial adsorbents and  $\omega$  is the content of a powder-like adsorbent in relative units.

Fig. 19 illustrates a graphic dependence of the porous composite mechanical strength on the aluminum transformation level.

Fig. 20 illustrates the structure of a porous body on the surface of a solid aluminum substrate in the shape of an intricate profile.

Fig. 21 illustrates the tools for evaluating the bonding pull strength between a porous layer and a solid substrate.

Fig. 22 illustrates the adsorption-desorption isotherms of nitrogen vapors on a porous composite of Al/Al<sub>2</sub>O<sub>3</sub> (1) and Al(OH)<sub>3</sub> (2).

Fig. 23 illustrates a SEM micrograph of a layer of Al(OH)<sub>3</sub>/Al having a thickness of nearly 0.2 mm for the aluminum transformation level of nearly 12% on the surface of a porous ceramic element.

Fig. 24 illustrates a sectional view of a capillary structure (a) with a large-pore ceramic element (b) positioned in a casing made of corrosion-resistance steel.

Fig. 25 illustrates a capillary structure comprising 24 peripheral vapor-discharge channels positioned throughout the casing perimeter.

Fig. 26 illustrates a SEM micrograph of a fracture of a porous composite produced on the base of aluminum powder.

Fig. 27 illustrates a microstructure of filamentary nanocrystals of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

Fig. 28 illustrates the desorption isotherms of benzene vapors by a porous composite Al/Al<sub>2</sub>O<sub>3</sub> (a) subjected to thermal treatment at 630(1), 900(2) and 1100°C(3) and the dependence of the specific surface and the sorption pore volume of a porous composite on the thermal treatment temperature (b).

Fig. 29 illustrates the body produced by a layered cross winding.

Fig. 30 illustrates microstructure of an aluminum hydroxide layer on a wire surface.

#### DETAILED DESCRIPTION AND MOST PREFERABLE EXAMPLES OF THE INVENTION

The following examples are described only for illustrative purpose but they do not impose any limitations on the invention filed for synthesis of composite porous materials with an anisotropic structure, wherein

the material of the composition  $\text{Al}/\text{Al}(\text{OH})_3$  fulfills simultaneously a structure-forming function and a consolidating one.

#### Example 1.

Aluminum powder of ACD-1 brand having an average particle size of 25-30  $\mu\text{m}$  was compressed or injected by means of vibratory loading into a detachable mold made of corrosion-resistance steel e.g. 12X18H9T, and a pre-formed powder was impregnated with an aqueous solution having  $\text{pH}=7.5$  in the volume of 0.95 of the pore volume of the resulting powder. A compacted briquette or a mold filled with powder were placed into a drying chamber and kept at the temperature from 85 to 95 $^{\circ}\text{C}$  for 2 hrs until water is fully vaporized. The synthesized material was dried in the air and a detachable mold was disassembled.

Figure 1 presenting a SEM micrograph of a fracture of a porous composite  $\text{Al}/\text{Al}(\text{OH})_3$  synthesized at the temperature from 85 to 95 $^{\circ}\text{C}$  for 2 hrs shows an aluminum nucleus encased by a porous shell of aluminum hydroxide (bayerite) having a thickness from 1 to 1.5  $\mu\text{m}$  and comprised of aggregated bayerite crystallites sized from 0.2 to 0.5  $\mu\text{m}$ . The neighboring shell does not contain any nucleus since it was left in an adjacent fragment of a destroyed sample. The inward surface of the shell is relatively smooth, while its outward part and the contact area are characterized by a rough and well developed surface due to the diffusion of aluminum monomer hydroxocomplexes of  $\text{Al}(\text{OH})_3$  through a porous bayerite layer and their bonding to an outward surface of a growing bayerite layer. The aggregation of aluminum particles during a chemical reaction process occurs without any visible variations in their shape and with no mechanical damage of a pre-formed porous structure. The macropores in a synthesized material actually present the voids formed between the composite particles of  $\text{Al}/\text{Al}(\text{OH})_3$  which have been packaged in a specified manner and coupled in the contact areas. The nanopores have been formed by bayerite crystallites coupled in the contact areas. Due to a heterogeneous chemical reaction and the formation of a porous material being conducted in a diffusion area, the aluminum-to-hydroxide transformation level and the mechanical compression strength of a porous composite  $\text{Al}/\text{Al}(\text{OH})_3$  do not exceed 0.15 to 0.2 and 10 to 15 MPa accordingly.

Figure 2 presenting a size distribution histogram of macropores illustrates a uniform size distribution of the pores due to a spherical shape of powder particles and the uniformity of their packaging. An average particle size of aluminum powder of ACD-1 brand makes up nearly 20  $\mu\text{m}$ , therefore an average size of macropores is in the range from 5 to 7  $\mu\text{m}$ . The above ratio is characteristic of the powder-based permeable materials produced by the powder metallurgy technique. The results of stereometric analysis quite well agree with the results of evaluating the maximum and average size of super-macropores according to GOST 25283-82. A gas permeability factor of a synthesized material made up nearly  $2.2 \times 10^{-13} \text{ m}^2$ , which corresponds to a permeability factor of the porous powder-based materials produced by sintering a bulk powder of ACD-1 brand. Figure 3, graph 1 illustrates an adsorption-desorption isotherm of benzene on a porous composite of  $\text{Al}/\text{Al}(\text{OH})_3$ . The isotherm in question is characterized by a specific hysteresis loop in a capillary condensation area at a relative pressure of  $p/p_s > 0.1$  and according to IUPAC classification could be related to type 2 [Greg S., Sing K. Adsorption, Specific Surface, Porosity. M., Mir. 1970. -p 407]. Due to low transformation level of aluminum the sorption pore volume is quite small, not exceeding 0.04  $\text{cm}^3/\text{g}$ .

The adsorption isotherms were used as the ground for calculating the pore size distribution (Fig. 4, graph 1). The graph has no maximum which is characteristic of industrial activated alumina and a pore size is within a very narrow range from 4.5 to 7.5 nm.

A porous aggregate on the surface of aluminum particles and in the contact areas (Fig. 1) is composed of bayerite crystallites (Fig. 5a) in the shape of irregular prisms having a size from 0.2 to 1  $\mu\text{m}$ . The presence of explicit reflexes on an electron-diffraction pattern (Fig. 5b) testifies in favor of a crystalline structure. The bayerite crystallites such as the ones resulting during its crystallization from the salt solutions [Dzisko V.A., Karnaukhov A.P., Tarasova D.V. *Physical-and-chemical Basis of Oxide Catalyst Synthesis*. – Novosibirsk: Nauka, 1978. - p 384] are not monocrystals but the crystalline aggregates of the primary particles having a spherical shape and the size up to 10 nm (Fig. 5b).

The thermal treatment of a porous composite at 550°C results in a full transformation of bayerite into activated alumina having a structure of parallel-positioned and densely packaged needle crystals of  $\gamma\text{-Al}_2\text{O}_3$  with lateral dimensions of nearly 5 nm and the length of nearly 100 to 150 nm (Fig. 6). The crystals of  $\gamma\text{-Al}_2\text{O}_3$  are probably coupled by the crystalline lattice defects causing the superposition of adjacent layers. The system of densely packed needle crystals forms a number of parallel-positioned capillaries having an evaluation diameter of nearly 5 nm.

The thermal treatment of bayerite deposits results in a respective increase of the sorption volume and the specific surface from 0.045 to 0.26  $\text{cm}^3/\text{g}$  (Fig. 3, graph 2) and from 53 to 368  $\text{m}^2/\text{g}$ . As it has already been noted such transformation of a porous structure is characteristic of aluminum hydroxide [Dzisko V.A. *Basic Methods of Catalyst Production*. – Novosibirsk: Nauka, 1983. – p 260] and is caused by the increase of the material actual density during dehydration.

#### Example 2.

Aluminum powder of ACD-1 brand having an average particle size from 25 to 30  $\mu\text{m}$  was compacted or injected by means of vibratory loading into a detachable mold made of corrosion-resistance steel, then impregnated with an aqueous solution having  $\text{pH}=11.5$  in the volume of 0.01 to 0.15 of the powder body pore volume and further placed into a drying chamber where it was kept at the temperature from 85 to 95°C for 1.5hrs until water is fully vaporized. Further the mold filled with powder was placed into a muffle furnace for the thermal treatment at the temperature of 550°C for 1 hr and cooled in the air.

The treatment in the above-described succession was performed 4 times (cycles).

An increase in a number of cycles causes an actually linear increase of the aluminum transformation level (Fig. 7), of the specific surface and the pore sorption volume (Fig. 8) which is imposed by the bulk increase of activated alumina thus produced due to elimination of the diffusion limitations resulting from the transformation of aluminum hydroxide into alumina. It means that the reaction products when subjected to crystalline chemical transformations on the one hand define the adsorption structural properties of a porous composite, while on the other they do not have any substantial influence on the kinetics of chemical interaction of aluminum with water and on the activities associated with the production of a highly disperse oxide system.

Figure 9 illustrates the adsorption isotherms of benzene on a porous composite of  $\text{Al}/\text{Al}_2\text{O}_3$  for aluminum transformation levels of 0.5(1) and 0.15(2). An isotherm portion at  $p/p_s$  of 0.8 to 1 passes almost parallel

to the axis  $p/p_s$  which is a proof of achieving an almost complete adsorption for this value of adsorbate relative pressure. An adsorption-desorption process is characterized by a hysteresis loop throughout the area of an isotherm rise. At  $p/p_s \approx 0.2$  a polymolecular adsorption is transformed into a capillary condensation. During the primary stages of a desorption process an isotherm is a slightly sloping one and then at  $p/p_s \approx 0.5$  exhibits a sharp slope until it converges with an adsorption isotherm. The loop of the kind is characteristic of adsorbents with through-capillaries having a substantially similar efficient radius (e.g. aluminum silicate). The shape of an adsorption isotherm for benzene vapors on the material under examination (the slope of adsorption-desorption branches, the width of a hysteresis loop, the value of  $p/p_s$  before a hysteresis starting point) does not exhibit any changes with variations of the active oxide content. According to IUPAC classification the isotherms in question could be related to type 2 [Greg S., Sing K. Adsorption, Specific Surface, Porosity. M., Mir. 1970.-p 407].

The pore size distribution calculated on the base of adsorption isotherms (Fig. 4, graph 2) for the transformation level of 0.5 appears to be similar for porous composites  $Al/Al_2O_3$  with different transformation levels. The graph has no maximum characteristic of industrial activated alumina and a pore size is within a very narrow range from 4.5 to 7.5 nm.

Figure 10 presents a SEM micrograph of synthesized composite ceramics illustrating different stages of a microstructure formation dependent on the aluminum transformation level. At first an aggregation accompanied by the formation of slightly explicit contacts has no visible effect on the surface morphology of particles (Fig. 10, a), while separate particles still preserve their structural peculiarity having the size and shape essentially similar to those of primary aluminum powder. The thickness of an oxide layer on aluminum particles is increased up to  $1\mu m$  with the increase of the transformation level, while the volume of a pre-formed oxide phase is increased so much that under the influence of mechanical strains thus produced the porous shells around aluminum particles are destroyed (Fig. 10 b, c). Should the transformation levels be further increased, the process of destruction of oxide shells becomes more intense (Fig. 10 d, e) which results in the formation of the coalescence of particles having the size and shape substantially different from the primary ones (Fig. 10, f). This in its turn causes the destruction of prior formed contacts and the formation of new ones. The portion of metallic aluminum is substantially decreased, and so is the macropore volume and the permeability factor, while the sorption pore volume is increased with a porous material structure becoming more similar as to its properties to the structure produced by colloid chemistry approaches. The total pore volume of the synthesized material is somewhat decreased with the increase of the transformation level.

Figure 11 illustrates the dependence of mechanical compression strength of a porous composite  $Al/Al_2O_3$  on the aluminum transformation level. With the increase of the transformation level the mechanical strength is increased from 6 to 40 MPA and further remains practically unchanged. It is evident that the strength of composite metal ceramics is defined by the number and quality of aluminum inter-particle contacts as well as their structure and properties which are generated during the crystallization from the solution and further thermal treatment. The use of the two competitive processes i.e. the formation of new contacts during the hydroxide deposition from the solution and the mechanical destruction of the "old" ones results in that the increase of composite ceramics mechanical strength is completed by the moment an intensive densification of a porous body is started.

## Example 3.

Granulated industrial adsorbents (zeolites NaX, NaY, NaA, activated alumina) were mechanically powdered and by means of a sieve device divided into small fractions. A resulting powder-like adsorbent was mixed with aluminum powder ACD-1 in mass ratio from 1:2 to 1:10, the mixtures were compressed or injected into a detachable mold made of corrosion-resistance steel, then impregnated with an aqueous solution having pH=10.0 in the volume of 0.95 of the pore volume of the pre-formed powder mixture. Then the mold filled with powder was placed into a drying chamber where it was kept at the temperature from 85 to 95° C for 1.5hrs until water is fully vaporized and further cooled in the air. A porous material in the mold was further impregnated with an aqueous solution having pH=8.0 in the volume equal to the material total pore volume and again placed into a drying chamber where it was kept at the temperature from 85 to 95° C for 2 hrs until water is fully vaporized. Then the mold filled with powder was placed into a muffle furnace for the thermal treatment at the temperature of 550°C for 1 hr and further cooled in the air.

A SEM study of the samples made it possible to visually estimate a structure, shape, size and nature of particle aggregations in a synthesized sorption material as well as the structure of the resulting inter-particle contacts. The texture of the samples in question was based on porous aggregates composed of adsorbent particles and aluminum particles, the latter having a substantially less size (Fig. 12). Adsorbent particles having an arbitrary fragment-like shape with wide planes of a brittle fracture produced during the dispersion of adsorbent granules are covered by the layer of aluminum particles and form the system of adsorbent/ $\text{Al}(\text{OH})_3/\text{Al}$ , wherein composite particles of  $\text{Al}(\text{OH})_3/\text{Al}$  are used as a binder, e.g., hydration hardening materials (cement, plaster). Aluminum particles are coupled with one another and with adsorbent particles by hydroxide contacts formed during the aluminum dissolution process and the deposition of its hydroxide in the area of inter-particle contacts. The material is characterized by a polydisperse structure and contains through-pores of the two types i.e. the spaces between coalesced aluminum particles and the spaces between porous aggregates. Merging with one another the chains of aluminum particles form an openwork locally ordered spatial frame having regularly alternating voids and particles. Some observed regions with irregular particle packaging are caused by a non-uniform thickness of an aluminum powder layer covering adsorbent particles due to the process disadvantages of the powder mixture forming and its loading into a mold.

The structure of contacts formed between aluminum particles as well as between aluminum particles and adsorbent particles (Fig. 10 c, d) presents the bundles of aluminum hydroxide aggregates which were formed as a result of crystallization from the solution. The contacts are characterized by a discrete nature imposed by a heterogeneous formation of crystallization centers, the growth of nuclei and the attachment thereto of new crystalline nuclei. The process of formation and growth of crystalline stage nuclei proceeds until the system reaches its thermal dynamic equilibrium and is stipulated by the solution super-saturation extent. As a result the phase (crystallization) contacts are formed between mixture particles with the structure of said contacts being similar to the structure of  $\text{Al}_2\text{O}_3$ -based adsorbents. It means that the formation of a porous structure of adsorbents and that of contacts are based on similar processes i.e. dissolution-crystallization.

Figure 13 illustrates the size distribution histograms of super-macropores in porous composites based on powder-like zeolite NaX (graph b) and activated alumina A-1 (graph a). The shape of histograms is characteristic of the materials having a polydisperse structure, in particular, of sintered powder materials.

The maximum and average efficient size of supermacropores depends first of all on the size of powder-like adsorbent particles, the packaging density of aggregates and also on the content of powder-like aluminum in the mixture. Should the content of aluminum be increased, a pore size and a permeability factor are decreased and when the aluminum content comes to 40 to 50% the hydraulic characteristics of synthesized ceramics approximate the characteristics of a porous composite  $\text{Al}_2\text{O}_3/\text{Al}$  due to said aluminum filling in supermacropores.

Table 1

## Hydraulic Properties of Synthesized Materials

Material Composition	Permeability Factor $K \times 10^{13}, \text{m}^2$	Maximum Pore Size $d_{\text{max}}, \mu\text{m}$	Average Pore Size $d_{\text{aver}}, \text{m}$
$\gamma\text{-Al}_2\text{O}_3$	2.8 ... 5.5	41...77	21...37.8
Zeolite+Al	5.6...6.6	58...89	26...38

Table 1 illustrates the results of studying the hydraulic characteristics of synthesized materials. A permeability factor and a pore size of composites are in conformity with similar characteristics of powder materials produced for example by sintering a free bulk bronze powder having a particle size of 0.16 to 0.2 mm. The values of a maximum and average pore diameter quite well agree with the stereometric study data.

Figure 14 illustrates the adsorption-desorption isotherms of benzene and water on a porous composite of zeolite  $\text{NaA}/\text{Al}/\text{Al}(\text{OH})_3$  (the composite was not baked to transform aluminum hydroxide into alumina) with various sizes of powder-like zeolite particles and the mass ratio of powder-like components 2:1. As it was noted above the adsorption of benzene vapors on primary powder-like zeolite is incurred with substantial difficulties, therefore the isotherm is slightly pronounced and passes in close proximity to the axis of relative pressures. The processes of benzene adsorption-desorption are characterized by a hysteresis loop throughout the area of an isotherm rise (Fig. 14a). A relatively smooth isotherm rise results from the presence of large pores, while the larger the pores the higher is the value of the relative pressure at which a capillary condensation takes place. At  $p/p_s$  of 0.2 a polymolecular adsorption turns into a capillary condensation. After a primary small rise of an isotherm the adsorption processes are carried at a substantially equal sloping angle to  $p/p_s$  axis, while at  $p/p_s$  of 0.4 to 0.6 their bending is observed with a further sharp rise up to  $p/p_s = 1.0$ . This is a proof of filling in small pores at relative pressures of  $p/p_s$  of 0.4 to 0.6. During the primary stages of a desorption process an isotherm is a slightly sloping one and then at  $p/p_s$  of 0.3 to 0.4 exhibits a sharp slope until it converges with an adsorption isotherm. The loop of the kind is characteristic of adsorbents with through-capillaries having a substantially similar efficient pore radius of 1.0 to 5.0 nm (e.g. aluminum silicate) which was confirmed by the calculation results. An S-shape of adsorption-desorption isotherms for benzene vapors on the samples under examination virtually is not changed for the samples having different fractional composition of powder-like zeolite. However, the slope of branches, the width of a hysteresis loop and the ultimate sorption pore volume largely depend on a particle size of zeolite NaA. Hence, the formation of a new porous structure during synthesis which is dependent on the packaging density of powder-like components and their distribution uniformity has a substantial effect on the adsorption nature of benzene vapors in the samples under examination. At the same time the adsorption-desorption isotherms of benzene vapors on a primary powder-like zeolite NaA and on synthesized components slightly differ from one another. Since water molecules easily penetrate the pores of zeolite NaA and the contribution of a new porous structure is small, the structural-adsorption

properties of a synthesized material are almost substantially defined by a zeolite structure. It should be noted that adsorption-desorption isotherms of water vapors on a composite of zeolite NaA/Al/Al(OH)<sub>3</sub> (Fig. 14,b) do not coincide throughout the interval of relative pressures. The ability of zeolites to the desorption of water and other polar adsorbates is defined not so much by the nature of a porous structure but by the chemical state of the surface, in particular, by the presence of Na and Ca cations in their adsorption cavities. The adsorption energy of water molecules is substantially different for a localized interaction with cations and for a dispersion interaction (for zeolite NaX respectively 40.2 kJ/M and 15.1 kJ/M). Such a large difference in the adsorption energy would also effect a thermal adsorption process. The amount of cations available for direct interaction with molecules adsorbed in zeolites NaA, NaX, CaX makes up approximately 3 mM/g. Assuming that a cation localization is provided by one water molecule, the amount of specifically adsorbed water makes up about 5 weight %. The total bulk of an adsorption space for zeolites in question makes up from 0.2 to 0.3 cm<sup>3</sup>/g and the ultimate value of water vapor adsorption from 20 to 30 weight %. The adsorption of zeolites in question should be provided at enhanced temperatures (over 300°C) with the withdrawal of the desorption moisture by means of degassing or purging with dry gas. The effect of an irreversible adsorption on alumina, aluminum silicates and mixed oxides was described in a number of papers and is related to a partial chemisorption of water by polar adsorbents [Ermolenko N.F., Efros M.D., Adjustment of Porous Structure of Oxide Adsorbents and Catalysts.-Minsk, Nauka and Technika.-1971.-p 280]. Adsorption and desorption branches of isotherms do not coincide either because during the process of adsorption changes the reaction of aluminum with water and the mass increase of the samples take place.

The examination results (Table 2, Fig. 15) show that the value of the sorption pore volume of a composite NaA/Al/Al(OH)<sub>3</sub> dependent on the mass fraction of aluminum powder in the mixture defined both for water vapors and benzene vapors passes through a peak and then exhibits a smooth slope when a mass fraction of aluminum powder is increased. As it was already discussed the values of V<sub>s</sub> defined for the adsorption-desorption of water vapors are almost two times higher than for benzene vapors. A peak of V<sub>s</sub> values for the benzene vapor adsorption appears to be more pronounced, since with the increase of an aluminum powder mass fraction in the mixture the value of the sorption pore volume is increased due to the contribution of a new porous structure produced during synthesis.

The adsorption isotherms of benzene and water vapors on a porous composite of NaY/Al/Al(OH)<sub>3</sub> have an essentially similar shape with a narrow hysteresis loop and very proximate values of the sorption pore volume (Fig. 16 a, b). An isotherm of primary powder-like zeolite NaY has the shape of a Langmuir type (Fig. 16 a). In the range of relative pressures from 0.1 to 0.9 it is characterized by a linear portion which is parallel to the axis of relative pressures, while the isotherm branches coincide for all values of p/p<sub>s</sub>. This proves the absence of a capillary condensation caused by the size comparability of benzene molecules and zeolite pores. The presence of a narrow hysteresis loop during the adsorption of benzene on a porous composite NaY/Al/Al(OH)<sub>3</sub> proves the influence of a new porous structure produced during the synthesis process. During water vapor adsorption the value of the sorption pore volume is slightly increased, and the width of a hysteresis loop is increased as a result of a small size of water molecules and more complete filling in of a material structure with water vapors. The lack of coincidence of isotherm branches during the adsorption-desorption of water vapors throughout the range of p/p<sub>s</sub> is also caused by

the chemisorption and by the increase of a sample mass as a result of aluminum chemically interacting with water.

Table 2

Influence of Zeolite:Al Ratio on Structural-adsorption Properties of Composite Ceramics of NaA/Al/Al(OH)<sub>3</sub>

Ratio of Zeolite:Al	Benzene			Water		
	Sorption Pore Volume, cm <sup>3</sup> /g	Specific Surface, m <sup>2</sup> /g	Efficient Pore Radius, nm	Sorption Pore Volume, cm <sup>3</sup> /g	Specific Surface, m <sup>2</sup> /g	Efficient Pore Radius, nm
1:2	0.142	92	3.1	0.267	477	1.0
1:3	0.160	-	-	0.284	-	-
1:5	0.140	-	-	0.298	-	-
1:10	0.115	-	-	0.284	-	-

The adsorption-desorption isotherms of benzene and water vapors on a porous composite containing activated alumina A-1/Al/Al(OH)<sub>3</sub> (Fig. 17 a, b) have a similar shape irrespective of the aluminum content in the mixture and are slightly different as to their total sorption pore volume. After an adsorption branch exhibits a sharp rise at  $p/p_s$  of 0.05 to 0.1 the process of a capillary condensation and monotonous filling in of the pores are observed. At  $p/p_s$  of 0.09 to 1 a porous structure is saturated by the adsorbate and at  $p/p_s$  of 0.02 to 0.4 the adsorption and desorption branches smoothly converge. In general, the structural-adsorption parameters of synthesized composite ceramics having different compositions are defined mainly by the sorption-active components (zeolites, alumina). Powder-like aluminum is used to combine powder-like adsorbents into a bound disperse body.

Table 3 illustrates the structural-adsorption properties of synthesized porous composites on the base of powder-like zeolites NaA, NaX, NaY, activated alumina A-1 and aluminum powder. The adsorption process depends on the adsorbate properties and the pore size of the materials under examination.

Table 3

Structural-adsorption Properties of Composite Ceramics

Composition	Zeolite Particle Size, mm	Benzene-Adsorbate			Water-Adsorbate		
		Sorption Pore Volume, cm <sup>3</sup> /g	Specific Surface, m <sup>2</sup> /g	Efficient Pore Radius, nm	Sorption Pore Volume, cm <sup>3</sup> /g	Specific Surface, m <sup>2</sup> /g	Efficient Pore Radius, nm
NaA (primary)	0.3 to 0.5	0.021	-	-	-	-	-
NaA+Al (mass ratio 2:1)	0.1 to 0.3	0.115	64	3.6	0.115	64	3.6
	0.3 to 0.5	0.1	48	2.9	0.1	48	2.9
	0.5 to 1.0	0.07	49	2.85	0.07	49	2.85
NaX (primary)	0.3 to 0.5	0.256	-	-	0.256	-	-
NaX+Al (mass ratio 3:1)	0.1 to 0.3	0.24	347	1.6	0.24	347	1.6
	0.3 to 0.5	0.23	294	1.6	0.23	294	1.6
	0.5 to 1.0	0.255	327	1.4	0.255	327	1.4
NaY (primary)	0.3 to 0.5	0.31	-	-	0.31	-	-



NaY+Al (mass ratio 3:1)	0.1 to 0.3	0.34	420	1.55	0.34	420	1.55
	0.3 to 0.5	0.26	391	1.33	0.26	391	1.33
	0.5 to 1.0	0.29	441	1.3	0.29	441	1.3
Al <sub>2</sub> O <sub>3</sub> (prim ary)	0.3 to 0.5	0.38	310	2.45	0.38	310	2.45
Al <sub>2</sub> O <sub>3</sub> +Al (mass ratio 3:1)	0.1 to 0.3	0.31	143	4.3	0.31	143	4.3
	0.3 to 0.5	0.28	204	2.75	0.28	204	2.75
	0.5 to 1.0	0.3	226	2.65	0.3	226	2.65

Since a diameter of a water molecule (nearly 0.26 nm) is substantially less than a diameter of a benzene molecule (nearly 0.6 nm) the adsorption of water vapors causes filling in of smaller pores which is impossible for benzene vapors. The size of the channels of dehydrogenated zeolite NaA makes up 0.42 nm, while in zeolites NaX and NaY it is 0.74 nm and as a result the benzene molecules freely penetrate the pores of the latter [Brek D. Zeolite Molecular Sieves. M., Mir, 1976.-p 780]. Therefore the results of a benzene and water adsorption for zeolites NaX and NaY are almost similar, while the values of sorption volume and specific surface of zeolite NaA for water vapors substantially exceed the respective parameters for benzene vapors and an average efficient pore radius for water vapors is lower. The examination results revealed a small dependence of specific surface and sorption pore volume on a granulometric composition of powder-like adsorbents. Probably the formation of a new porous structure by the synthesis procedure depends on the packaging density of powder-like components and their distribution uniformity. Since the contribution of a porous composite structure Al/Al(OH)<sub>3</sub> into structural-adsorption properties of composite ceramics is very small, the sorption pore volume and the specific surface of composites are almost fully dependent on the properties of primary industrial adsorbents and also by the mass ratio of powder-like adsorbent and aluminum powder.

Figure 18 illustrates the isolines of mechanical compression strength for porous composites in  $r - \omega$  coordinates where  $r$  is a particle size of powder-like industrial adsorbents and  $\omega$  is the content of a powder-like adsorbent in relative units. The increase of the particle size of powder-like zeolite (Fig. 18 a) or activated alumina (Fig. 18 b) or their content in a composite material reveals a general tendency towards the impairment of mechanical strength of synthesized porous composites from 7 to 2 MPa. This could be explained by the fact that mechanical strength depends not only on the quality of the contacts but also on the number of said contacts per unit of a porous body destruction area. The decrease of a mass fraction of powder-like aluminum and the increase of a particle size of a powder-like adsorbent result in the decrease of the number of contacts and hence to the decrease of mechanical strength. It should be noted that the process of growing the contacts between particles of powder-like components and hence their mechanical strength are limited by the concentration of aluminum hydroxocomplexes in the solution.

The concentration of hydroxocomplexes in its turn depends on the aluminum dissolution rate, which is limited as a result of the formation of reaction solid products on the surface of aluminum particles and the process transfer into a diffusion region.

The use of cyclic treatment in accordance with example 2 makes it possible to adjust the mechanical strength of porous composites on the base of powder-like zeolite /Al/Al<sub>2</sub>O<sub>3</sub> and activated alumina /Al/Al<sub>2</sub>O<sub>3</sub>. Figure 19 illustrating a graphic dependence of the mechanical strength of porous composites on the aluminum transformation level shows the growth of their mechanical strength with the increase of

α. Composites containing powder-like adsorbents having minimum-sized particles and a maximum mass fraction of aluminum powder exhibit most intensive increase of their mechanical strength (up to 30 MPa). The total pore volume of the materials under examination is in the range from 0.43 to 0.63 cm<sup>3</sup>/g and remains virtually unchanged with the increase of the aluminum transformation level.

It is known that mechanical strength of bound disperse systems of a globular type is determined by the adhesive forces of particles in their contact areas also by the strength of separate inter-particle contacts and by the number of the latter per unit of a destruction area. [Schukin E.D., Pertsov A.V., Amelina E.A. Colloid Chemistry. M., MGU, 1982.-p 348; Frolov Ju.G. Colloid Chemistry Course. Surface Effects and Disperse Systems. Textbook for Higher School.- Second Edition, Revised and Added.-M.:Chimija, 1988.- p 464)

The calculated values of the adsorbent mechanical strength make up to 10<sup>2</sup> MPa and more dependent on the dispersion, porosity and on the average theoretical strength of a separate phase (crystallization) contact, i.e. dependent on the material chemical nature and physical-and-chemical strength of the adsorbents. However, the actual strength of industrial high-disperse oxide materials is one order lower. Mechanical tests for a number of industrial adsorbents and catalyst carriers are described [Bessonov A.I., Schukin E.D.//Kinetics and Catalysis, 1970, Vol. 11, No. 1, pp. from 215 to 218]. It was stated that mechanical strength of industrial zeolites CaA, NaA and activated alumina is varied in a wide range from 3 to 15 MPa and depends on the nature of separate contacts and their number per unit of a contact cross-section which in its turn depends on the structure dispersion and geometric peculiarities.

Sintering of high-disperse oxide systems results as a rule in the increase of their strength but at the same time it causes the decrease of porosity, specific surface, pore volume and the increase of an average pore radius. Sintering of black copper oxide samples [Tsikozal L.T., Tarasova D.V., Fenelonov V.B. Kinetics and Catalysis, 1979, Vol.21, No. 5, pp 947 to 953] and those of silica gel [Dzisko V.A., Tarasova D.V., Vishnjakova G.P. Kinetics and Catalysis, 1967, Vol.8, No. 1, pp 193 to 197] baked at the temperatures up to 900<sup>0</sup>C results in the increase of inter-particle contacts and mechanical strength from 2 to 5 MPa up to 13.5 to 26 MPa. However, during the first sintering stages not only overgrowing of the contact areas takes place but also the transfer of the substance from loosely packaged portions to the densely packaged ones, this causing the decrease of the number of contacts in the material bulk. The mechanical strength at that remains constant or even somewhat decreases. A number of authors [Gagarina V.A., Kuklina V.I., Khomjakova L.G. et al. Kinetics and Catalysis, 1972, Vol.13, No. 1, pp 174 to 179] having considered the changes of aluminum porous structure in a wide temperature range (from 800 to 1400<sup>0</sup>C) came to the conclusion that a thermal treatment temperature has a substantial effect on the variations of the material specific surface, pore volume and radius, but virtually has very little influence on its mechanical strength. While the rise of temperatures causes the decrease of specific surface in 30 times and the increase of a pore radius in 14 times, the value of mechanical strength is varied in the range from 4 to 7 MPa having a tendency to be somewhat decreased with the temperature rise. The pore volume at that is smoothly decreased from 0.53 to 0.23 cm<sup>3</sup>/g.

High values of mechanical strength of synthesized composite ceramics prove that during the synthesis process (using cyclic treatment) in the area of inter-particle contacts there is a constant supply of "constructional material" i.e. aluminum hydroxocomplexes from a supersaturated solution and their inclusion into a lattice of contacting zeolite particles (activated alumina) and a hydroxide shell surrounding

aluminum particles. Crystallization from a supersaturated solution results in the appearance of crystallization contacts between adjacent small crystals. Table 4 shows the results of studying the influence of the porosity of synthesized ceramics on its mechanical strength. The increase of the aluminum transformation level (number of treatment cycles) results in just slight changes of the total pore volume but causes a substantial increase of the mechanical strength. Hence, the number of contacts remains virtually unchanged but their radius is increased due to the constant supply and deposition of aluminum hydroxocomplexes in the contact area.

The foregoing examples 1 to 3 illustrate the advantages of the invention for the adjustment of structural and mechanical properties of high-disperse oxide systems (adsorbents and catalyst carriers) and for the production of composite porous materials having different chemical compositions.

#### Example 4.

A slurry is prepared on the base of aluminum powder ACD-1 and volatile organic solvent, e.g. acetone by mechanical stirring of liquid with powder. If necessary the slurry could contain porous or nonporous particles of non-organic materials, e.g. powder-like zeolite and/or activated alumina.

The coating is deposited by the immersion of a substrate pre-heated up to 40 to 60°C (solid aluminum or porous non-organic substance) into a bath at constant stirring of the slurry and a constant rate of extraction to provide a uniform thickness coating. The heat that has been accumulated provides adhering of powder particles to the product surface and the formation of a thin porous layer on the whole or on a fraction of a substrate surface.

A metal surface could be contaminated by various impurities like organic oils and grease, wax, resins, non-organic carbon deposits, oxides etc. therefore pre-treatment of the surface is required (degreasing with organic solvents and alkali compounds or by means of ultrasonic degreasing apparatus).

Surface coating could also be performed by spraying or spreading, however, the use of fluid deposition technique makes it possible to provide a homogeneous coating having a thickness from 10 to 150 µm. The coating thickness depends on the slurry viscosity i.e. the mass ratio of fluid and disperse material, therefore if a surface coating is deposited by dipping it is necessary to provide rigid control of these parameters.

Table 4

Dependence of Composite Ceramics Mechanical Strength on Total Pore Volume

Composition	Total Pore Volume, cm <sup>3</sup> /g	Mechanical Strength, MPa
Al/Al <sub>2</sub> O <sub>3</sub>	0.2	39.0
	0.22	37.5
	0.24	27.5
	0.26	10.0
Zeolite NaA/Al/Al <sub>2</sub> O <sub>3</sub>	0.4	28.4
	0.42	25.2
	0.44	14.8
	0.45	8.0
Activated Alumina/Al/Al <sub>2</sub> O <sub>3</sub>	0.4	24.8
	0.42	23.2
	0.44	12.0
	0.45	9.8

After evaporation of the solvent the treatment of a substrate with a pre-deposited layer was performed with an aqueous solution having pH=9.0 at the maximum temperature of 100° C for 2 hrs to provide a chemical reaction of aluminum with an aqueous solution and a complete or partial dissolution of primary disperse aluminum (depending on a characteristic size of primary particles). At the same time the dissolution of compacted aluminum takes place with the formation of a supersaturated solution of monomer aluminum hydroxocomplexes  $Al(OH)_4$ . The mass crystallization of aluminum hydroxide (bayerite or boehmite) from the solution is performed by the attachment of hydroxocomplexes to the surface of growing hydroxide nuclei and in the contact area between bayerite crystallites coming into contact. This is how a porous material composed of  $Al(OH)_3/Al$  is formed including its bonding to the surface of solid aluminum (substrate) by phase contacts formed.

Figure 20 illustrates the structure of a porous body in the shape of an intricate profile on the surface of a solid aluminum substrate. SEM micrographs illustrate a system of densely packaged crystallites formed on the surface of primary aluminum particles and on the surface of a solid aluminum substrate and coupled by phase contacts. The surface structures of aluminum particles and a solid substrate are similar (Fig. 18 c, d) which proves the similarity of interaction processes of disperse and solid aluminum with an aqueous solution having pH=7.5-11.5.

The pull strength of the bond between a porous layer and a solid substrate was defined by means of a testing device (Fig. 21) and made up nearly 2 MPa.

A porous layer is resistant to thermal shocks and is not peeled off a solid substrate. The results of studying the samples at a mesopore structural level are shown in Fig. 22. The isotherms of low-temperature nitrogen adsorption-desorption by bayerite dried under standard conditions (sample 1) and then baked at 650°C for 2 hrs (sample 2) have a characteristic feature of sorption isotherms of type IV i.e. a hysteresis loop in the area of multi-layer adsorption that is associated with a capillary condensation in mesopores having a size of  $2 \text{ nm} \leq d \leq 50 \text{ nm}$  which makes it possible to consider the samples in question basically as mesopore ones. The shape of a hysteresis loop H3 for both isotherms is characteristic of dehydrated bayerite [De Boer J.H., Lippens B.C.//J. Catal. 1964 Vol. 3 p38]. This is usually related to the presence in the texture of narrow slot-like mesopores formed by blade particles or by the coalescence of particles. The calculated values of specific surface and pore volume depend on dehydration conditions of the samples accompanied by inadequate loss of aqua-and hydroxide groups and resulting in the damage of a surface layer integrity. So sample 1 has the specific surface of 81.30  $\text{m}^2/\text{g}$  according to BET, the pore volume of 0.0661  $\text{cm}^3/\text{g}$  according to BDH, an average pore diameter of 8.68 nm, a prevailing mesopore diameter of 4.0 nm, while similar characteristics for sample 2 make up accordingly 70.52  $\text{m}^2/\text{g}$ , 0.1239  $\text{cm}^3/\text{g}$ , 8.62 nm and 3.52 nm. Mesostructures of samples 1 and 2 in Fig. 20 are slightly different from one another, therefore it could be concluded that directional coalescence of primary aluminum hydroxide particles during the hydration hardening of metal powder is preserved during the subsequent thermal treatment. Expansion of a hysteresis loop and an almost 2 times increase of the pore volume of a baked sample as compared to a dried one is related to the growth of dehydration pores.

Example 4 illustrates the possibilities of the invention for the production of capillary structures of heat pipes in the form of a thin layer on the inward surface of an aluminum profile. A similar structure could be formed on a flat aluminum sheet, for example, as a catalyst carrier in the production of catalytic reactors.

## Example 5.

Ceramic or titanium powder was subjected to radial pressing out to produce a porous pipe-shaped element having respectively the outward and inward diameters of 16 and 8 mm, the porosity of nearly 50% and a pore size from 120 to 150  $\mu\text{m}$ . A porous element was baked in the air (porcelain) or in argon (titanium) at the temperature of nearly  $1250^{\circ}$  followed by covering the whole of the surface or a fraction thereof by dipping, spraying or spreading with a slurry containing aluminum powder of ACD-1 brand having an average particle size from 25 to 30  $\mu\text{m}$  which resulted in the element pore channels being filled with powder at the depth from 1 to 1.5 of an element pore diameter. Further the porous element with a pre-deposited aluminum powder layer was treated with an aqueous solution having  $\text{pH}=7.5$  at the maximum temperature of  $100^{\circ}\text{C}$  for 2 hrs. All the processes described in examples from 1 to 4 are conducted during the treatment process except for the formation of phase contacts between a porous material composed of  $\text{Al}(\text{OH})_3/\text{Al}$  and a titanium element.

Figure 23 illustrates a SEM micrograph of a material layer  $\text{Al}(\text{OH})_3/\text{Al}$  having a thickness of nearly 0.2 mm for the aluminum transformation level of nearly 12% on the surface of a porous ceramic element. The permeability factor of the ceramic element makes up nearly  $10^{-9}\text{m}^2$  and a pore size from 120 to 150  $\mu\text{m}$ , while the permeability factor of the layer composed of  $\text{Al}(\text{OH})_3/\text{Al}$  makes up  $3.5 \times 10^{-13}\text{m}^2$  and a pore size from 4.5 to 7.5  $\mu\text{m}$ . Hence, the resulting composite material has an explicit anisotropic structure.

The element with a pre-deposited layer  $\text{Al}(\text{OH})_3/\text{Al}$  was placed into a divided mold, while the spaces between said element and said mold were filled with disperse aluminum using vibration compacting (any other method of forced filling, or a slurry on the base of disperse aluminum can be used). Further a pre-formed porous body was impregnated with a water solution having  $\text{pH}=7.5$  in the volume of 0.5 of the pre-formed material pore volume. A pre-formed porous body impregnated with the solution was placed into a drying chamber at the maximum temperature of  $100^{\circ}\text{C}$  to provide a chemical reaction between said aluminum and said solution for 2hrs. After cooling a porous material still in the mold was impregnated with a water solution having  $\text{pH}=7.5$  in the volume equal to the material total pore volume and placed into the drying chamber at the temperature from 85 to  $95^{\circ}\text{C}$  where it was kept for 2 hrs until water is fully vaporized. Then the mold with powder was placed into a muffle furnace where it was subjected to a thermal treatment at  $550^{\circ}$  for 1 hr and cooled in the air. The transformation level of disperse aluminum until its full transformation into hydroxide is controlled by means of cyclic treatment according to Example 2.

The production of capillary structures for heat pipes always entails difficulties caused by the formation of an anisotropic porous structure. Another problem is the conjugation of capillary structures with a vaporizer casing which is to ensure a reliable thermal contact of capillary structures with the casing. The most reliable thermal contact is provided by means of burning the capillary structures to the heat pipe casing. However, it is not always possible to use the casing made of the same material as the capillary structures. Besides, it is practically not possible to provide a nonshrinking sintering of powder which results in the detachment of the capillary structures from the casing. Pressing the capillary structures into a heat pipe casing, firstly, does not always ensure a reliable thermal contact due to possible geometry irregularities at the application of pressures, secondly, it leads to the substantial technical problems especially when large-length capillary structures are concerned. The invention filed makes it possible to provide a reliable thermal contact of capillary structures with the casing since the formation of a porous

structure having a composition of  $\text{Al}(\text{OH})_3/\text{Al}$  and its bonding to porous elements and thus interconnection of said elements is performed directly in a heat pipe casing.

Fig. 24 illustrates a cross-section of a capillary structure (a) with a large-sized ceramic element (b) placed into a casing of corrosion-resistant steel. A capillary structure is comprised of 24 peripheral steam-discharge channels positioned throughout the casing perimeter (Fig. 25) and 1 central steam-discharge channel. All the channels are formed by respective setup elements. All peripheral channels are closed on the outlet side of main channels and vice versa. The invention filed is advantageous in that it provides the possibility to produce capillary structure of any shape and to close the channels at any required depth.

#### Example 6.

Aluminum powder of ACD-1 brand having an average particle size from 25 to 30  $\mu\text{m}$  was compressed or injected by means of vibratory loading into a detachable mold made of corrosion-resistance steel, impregnated with an aqueous solution having  $\text{pH}=10.0$  in the volume of 0.1 to 0.15 of the pore volume of a powder body and further placed into a drying chamber where it was kept at the temperature from 85 to 95 $^{\circ}\text{C}$  for 2 hrs until water is fully vaporized with further cooling in the air. Then a porous material was impregnated with an aqueous solution having  $\text{pH}=7.5$  in the volume equal to the material total pore volume and placed into the drying chamber at the temperature from 85 to 95 $^{\circ}\text{C}$  where it was kept for 2 hrs until water is fully vaporized. Further the mold with the powder was placed into a muffle furnace where it was subjected to a thermal treatment at 550 $^{\circ}$  for 1 hr and cooled in the air. Treatment in the above-described succession was performed 7 times (cycles). Then a synthesized material was subjected to a thermal treatment at 750 to 1450 $^{\circ}\text{C}$ . Thermal treatment results in polymorphous transformations of alumina, its sintering, melting and evaporation and also in the growth of filamentary crystals of alumina  $\alpha\text{-Al}_2\text{O}_3$  caused by the domination of a vapor-phase mechanism.

Figure 26 presenting a SEM micrograph of a fracture of a porous composite illustrates the totality of alumina spheres coupled in the contact areas by oxide bridges.

The compression strength of the material makes up from 100 to 120 MPa. Both on the outward and inward surfaces of oxide shells there is formed a system of plaited corundum crystals having a thickness of nearly 100 nm and the length up to 2  $\mu\text{m}$  (Fig. 27, a, b).

Figure 28a illustrates the adsorption-desorption isotherms of benzene vapors on a porous composite of  $\text{Al}/\text{Al}_2\text{O}_3$  (a) subjected to a thermal treatment at various constant temperatures for 1 hr. An adsorption-desorption process is characterized by a hysteresis loop throughout the area of an isotherm rise. At  $p/p_s = 0.15\ldots 0.2$  a polymolecular adsorption is transformed into a capillary condensation, and an isotherm portion at  $p/p_s = 0.8\ldots 1$  passes almost parallel to the  $p/p_s$  axis which is a proof of achieving an almost complete adsorption for this value of an adsorbate relative pressure. During the primary stages of a desorption process an isotherm is a smoothly sloping one and then at  $p/p_s \approx 0.5$  exhibits a sharp slope until it converges with an adsorption isotherm.

The loop of the kind is characteristic of adsorbents with through-capillaries having a substantially similar efficient radius (e.g. aluminum silicate). According to IUPAC classification the isotherms in question could be related to type 2.

The results of structural-adsorption studies were taken as the basis for calculating the values of specific surface, sorption volume and efficient pore radius. Fig. 28b illustrates the graphic dependence of specific surface  $S_w$  and sorption pore volume  $V_s$  on the thermal treatment temperature of a porous composite  $Al/Al_2O_3$ . A slight increase of the values  $S_w$  and  $V_s$  observed in the temperature range from 600 to 700°C could be explained by the aluminum oxidation with the resulting formation of high-disperse  $\gamma-Al_2O_3$ . At a further temperature increase due to sintering of  $Al_2O_3$  the values of  $S_w$  and  $V_s$  start to decrease, while each is decreased at a different rate dependent on the thermal treatment temperature. The sorption pore volume exhibits small changes up to the temperature of 800°C but further it starts to decrease very fast making up nearly 20 m<sup>2</sup>/g at 1200°C. An efficient pore radius is slightly increased from 4 to 5.4 nm within the temperature range in question.

The stability of a composite material at high temperatures could be used for the production of high-temperature catalysts.

#### Example 7.

A method of producing porous materials is based on determination the similarity of the formation processes of aluminum hydroxide and that of alumina on the surface of aluminum bodies irrespective of their geometric shape and size (Fig. 20 c).

A cylinder-shaped winding body was formed (Fig. 29). An aluminum ADO wire having a diameter of 0.2 mm was cross wound at the angle of 30° in 40 layers on a former fixture having a diameter of 10 mm and the length of 320 mm. This stage provided the regularity of a porous body macrostructure having the cells in the form of curvilinear rhombs. Further a pre-formed winding body was subjected to a radial pressing out at the pressure of 50 MPa by means of a dry isostatic pressing device [Petjushik E.E., Reut O.P., Jakubovsky A.Ch. Deformation Basis of Wire Winding Bodies.-Minsk.: UP "Technoprint", 2003.-p.218]. The resulting billet had the following dimensions: the length of 320 mm, an internal diameter of 10 mm, an external diameter of 16 mm. The mechanical strength of the billet is provided by plastic inter-particle contacts and by increasing the rigidity of each turn due to the wire bending deformation in inter-contact spans. The billet was removed from the winding body and impregnated with an aqueous solution having pH=11.5 in the volume of 0.1 to 0.15 of the powder body pore volume and further placed into a drying chamber where it was kept at the temperature from 85 to 95°C for 1.5hrs until water is fully vaporized with further cooling in the air. Then a porous material was impregnated with an aqueous solution having pH=7.5 in the volume equal to the material pore volume and placed into the drying chamber at the temperature from 85 to 95°C where it was kept for 2 hrs until water is fully vaporized. Treatment in the above-described succession was performed 3 times.

During the above procedure a surface layer of an aluminum wire was partially transformed into aluminum hydroxide. A pre-formed tube-shaped biporous product exhibited the following characteristics: the macrostructure porosity of 50%, an average macrostructure pore size of 110 μm, the thickness of an aluminum hydroxide layer on a wire surface of evaluated 1.5 μm, an average microstructure pore size of evaluated 5 nm (Fig. 30). A mechanical wire contact of the neighboring turns is added with phase contacts of crystallite aggregates of aluminum hydroxide ( $Al(OH)_3$  or  $AlOOH$ ) which results in the increase of mechanical strength of a porous composite material on the whole. The increase of a microporous layer thickness on a wire surface could be achieved by the anneal cycling (550°C) of the

billet and by the treatment with an aqueous solution having pH=7.5-11.5 in the volume equal to the material pore volume at the temperature from 85 to 95°C.

The following technique is a variety of the above-described approach. A winding body (See Fig. 29) produced by a layered cross winding of aluminized (covered by an aluminum layer) wire on a rigid (steel) former fixture plated with an elastomer layer is treated with an aqueous solution having pH=11.5 which results in a partial or complete transformation of aluminum into aluminum hydroxide  $\text{Al}-\text{Al}(\text{OH})_3$ . The transformation of the kind [Porous Composites on the Base of Aluminum-Oxide Cermets. Synthesis and Properties / Tikhov S.F., Romanenkov V.E., Sadjikov V.A., Parmon V.N., Patko A.I. //Novosibirsk: Publishing House CO RAN, Subsidiary of "Geo", 2004.-p 205] is accompanied by the formation on a wire surface starting from peripheral portions of an aluminum hydroxide layer (having a somewhat increased bulk as compared to a primary aluminum bulk) which forms porous contacts between the turns in the contacting areas of primary winding body wires. Thus, a bound biporous body is produced having a macrostructure formed by the turns of a winding body, wherein the formation of wire-frame properties of a wire biporous material (product) is provided due to the growth of oxide bridges in the contact areas of wire turns, and a microstructure is formed as a porous layer on the surface of aluminum wire, should aluminum be partially transformed into aluminum hydroxide, or in the form of a small-pore structure in the bulk of a primary wire, should the wire aluminum be fully transformed into aluminum hydroxide. As an aluminized wire is used, only an aluminum layer used for plating the wire is fully or partially transformed into hydroxide with the resulting formation of porous contacts between the turns and of a porous aluminum hydroxide layer throughout the whole free surface of a wire. The frame of a biporous body in this case is formed by the material of a primary wire. In all cases the aluminum-to-hydroxide transformation level is defined by the time a billet is treated with an aqueous solution having pH=7.5-11.5 and by the number of treatment cycles. A biporous body macrostructure has the least density when aluminum is partially transformed into hydroxide.

Treatment of a deformed winding body with an aqueous solution having pH=7.5-11.5 provides the possibility to control a macrostructure of a resulting biporous body by the changes of a winding body density during the process of radial pressing out. The method facilitates the production of a much denser macrostructure of a biporous body as compared to the above-described one. A method contemplating a radial pressing out or a radial expanding of a winding body after aluminum is partially transformed into hydroxide on the surface of an aluminum wire followed by a subsequent final treatment with an aqueous solution having pH=7.5-11.5 with a partial or complete transformation of aluminum into hydroxide makes it possible to produce the most dense macrostructure of a biporous body since the process of an intermediate pressing out (expanding) results in a partial destruction of a hydroxide porous layer and its filling in with billet macropore particles (a winding body). A final treatment with an aqueous solution having pH=7.5-11.5 of a billet results in the consolidation due to newly formed porous contacts between wire turns.

A method filed makes it possible to produce permeable and partially permeable products from composite materials  $\text{Al}-\text{Al}(\text{OH})_3$  – metal,  $\text{Al}_2\text{O}_3$  – metal. A macrostructure of finished products in this case is formed mainly during the production of wire winding bodies and their pressure treatment. The required regularity of a macrostructure is provided due to precise positioning of the wire turns during the formation of a winding body. A predicted variation of a macrostructure pore size is achieved due to a regular layer-to-



layer variation of a lateral dimension and a wire cross-sectional shape. All this makes it possible to achieve a pre-defined anisotropic macrostructure of a product material. The porosity of a macrostructure is adjusted during a radial pressing out (expanding) of a winding body by varying the swaging pressures. The volume of a microporous (nanoporous) material as a portion of a biporous product is defined by the working modes of the billet treatment with an aqueous solution having pH=7.5-11.5 and by the number of treatment cycles.

In all cases a porous body could be heated up to the temperature of aluminum hydroxide dehydration in the air followed by the cooling to produce  $\gamma\text{-Al}_2\text{O}_3$ . Such thermal treatment could be performed in a number of cycles. Besides, a subsequent thermal treatment of a synthesized material is possible at 750 to 1450°C. This thermal treatment results in polymorphous transformations of alumina, its agglomeration, melting, vaporization and also in the growth of thread-like crystals  $\alpha\text{-Al}_2\text{O}_3$  conditioned by the domination of a vapor-phase mechanism.

Thus, wire structures are greatly promising as the basis for the production of polyporous permeable materials since they primarily possess an adjustable regular structure which is a kind of a "template" of a polyporous body macrostructure. It is technically feasible to produce a new class of polyporous products having a regular macrostructure and pre-defined macrostructure properties on the surface of structure-forming elements. The possibility of adjusting the basic properties of the products thus produced is also provided.

## CLAIMS

1. A synthetic composite gas-and-fluid permeable material in the form of a solid with a porous-open structure of crystallite aggregates of aluminum hydroxide ( $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$ ) or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) coupled by phase contacts, wherein said material is made with the specific surface from 50 to 200  $\text{m}^2/\text{g}$  and the space between said crystallites presents pores having a diameter from 4.5 nm to 100  $\mu\text{m}$ , while said material is synthesized by the dissolution of disperse aluminum in an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  at the maximum temperature of  $100^\circ\text{C}$  (preferably from  $85$  to  $95^\circ\text{C}$ ) followed by the mass crystallization of aluminum hydroxide from a supersaturated solution of aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts.

2. The material as in claim 1, wherein said material could additionally comprise separate aluminum particles surrounded by porous shells composed of crystallite aggregates of aluminum hydroxide ( $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$ ) or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) and coupled by phase contacts in the form of crystallite aggregates having a similar structure.

3. The material as in claim 1, wherein the size of the resulting crystallites makes up from 200 to 1000 nm.

4. The material as in claim 1, wherein said material is synthesized from disperse aluminum pre-formed by any arbitrary means or from a powder-like material coated by an aluminum layer.

5. The material as in claim 4, wherein the dissolution of aluminum during the material synthesis is provided in the process of a heterogeneous chemical reaction of aluminum with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$ .

6. The material as in claims from 1 to 5, wherein the dissolution of aluminum during the material synthesis is provided by means of impregnating a pre-formed powder with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  in the volume of 0.01 to 0.95 of the pore volume of powder media.

7. The material as in claims from 1 to 6, wherein the dissolution of aluminum during the material synthesis is provided by means of the thermal treatment of pre-formed powder with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  at the temperature from  $85$  to  $95^\circ\text{C}$  for 1.5-2 hrs until water is fully vaporized.

8. The material as in claims from 1 to 7, wherein an additional dissolution of aluminum during the material synthesis is performed by means of impregnating a cooled pre-formed porous body with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  in the volume equal to the material pore volume.

9. The material as in claims from 1 to 8, wherein an additional dissolution of aluminum during the material synthesis is performed by means of the thermal treatment of a pre-formed porous body impregnated with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  at the temperature from  $85$  to  $95^\circ\text{C}$  for 1.5-2 hrs until water is fully vaporized.

10. The material as in claim 9, wherein said material is characterized by an adsorption-desorption isotherm shown in Fig.3, graph 1 and a pore size distribution shown in Fig. 4, graph 1.

11. The material as in claim 1, wherein said material is additionally subjected to a thermal treatment at the temperature from  $450^\circ$  to  $550^\circ\text{C}$  until aluminum hydroxide is fully transformed into alumina.

12. The material as in claim 11, wherein said material is characterized by a microstructure shown in TEM micrograph (Fig. 6).

13. The material as in claim 11, wherein said material is characterized by an adsorption-desorption isotherm shown in Fig. 3, graph 2.

14. The material as in claims from 1 to 13, wherein the above-described procedures are performed a number of cycles during the material synthesis.

15. The material as in claim 14, wherein said material is characterized by the structural dependence on the aluminum transformation level shown in SEM micrograph Fig. 10.

16. The material as in claim 14, wherein said material is characterized by an adsorption-desorption isotherm shown in Fig. 9, graph 1 for the aluminum transformation level of 0.5.

17. The material as in claim 14, wherein said material is characterized by the dependence of the aluminum-to-alumina transformation level on the number of cycles shown in Fig. 7.

18. The material as in claim 14, wherein said material is characterized by the dependence of its specific surface and sorption pore volume on the number of cycles shown in Fig. 8.

19. The material as in claim 14, wherein said material is characterized by the dependence of the mechanical strength on the number of cycles shown in Fig. 11.

20. A synthetic composite gas-and-fluid permeable material in the form of a solid with a porous-open structure of crystallite aggregates of aluminum hydroxide ( $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$ ) or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) coupled by phase contacts, wherein said material is made with the specific surface from 50 to 450  $\text{m}^2/\text{g}$  and comprised of metallic organic and/or inorganic, non-porous and porous disperse particles of various configurations and/or continuous fibers (threads) coupled by mechanical and/or phase contacts in the form of crystallite aggregates of aluminum hydroxide ( $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$ ) or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ), and the space between said crystallites and said disperse particles presents pores having a diameter from 4.5 nm to 360  $\mu\text{m}$ , while said material is synthesized by the dissolution of disperse aluminum in an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  at the maximum temperature of  $100^\circ\text{C}$  (preferably from 85 to  $95^\circ\text{C}$ ) followed by the mass crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts.

21. The material as in claim 20, wherein said material additionally comprises separate aluminum particles surrounded by porous shells composed of crystallite aggregates of aluminum hydroxide ( $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$ ) or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) and coupled by phase contacts in the form of crystallite aggregates having a similar structure.

22. The material as in claim 20, wherein said material is synthesized from a mixture pre-formed by any arbitrary means and comprising metallic organic and/or inorganic, non-porous and porous disperse particles of various configurations and/or continuous fibers (threads) and disperse aluminum or other disperse material coated by an aluminum layer.

23. The material as in claim 20, wherein the dissolution of aluminum during the material synthesis is provided in the process of a heterogeneous chemical reaction of aluminum with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$ .

24. The material as in claims from 20 to 23, wherein the dissolution of aluminum during the material synthesis is provided by impregnating a pre-formed porous body with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  in the volume of 0.01 to 0.95 of the pore volume of a pre-formed mixture.

25. The material as in claims from 20 to 24, wherein the dissolution of aluminum during the material synthesis is provided by the thermal treatment of a pre-formed mixture impregnated with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  at the temperature from 85 to  $95^\circ\text{C}$  for 1.5-2 hrs until water is fully vaporized.

26. The material as in claims from 20 to 25, wherein an additional dissolution of aluminum during the material synthesis is provided in the process of a heterogeneous chemical reaction of aluminum with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  in the volume equal to the material pore volume.

27. The material as in claim 26, wherein an additional dissolution of aluminum during the material synthesis is provided by the thermal treatment a pre-formed porous body impregnated with an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  at the temperature from  $85$  to  $95^{\circ}\text{C}$  for  $1.5\text{-}2$  hrs until water is fully vaporized.

28. The material as in claim 20, wherein said material is additionally subjected to a thermal treatment at the temperature from  $450^{\circ}$  to  $550^{\circ}\text{C}$  until aluminum hydroxide is fully transformed into alumina.

29. The material as in claim 20, wherein said material is made from the mixture of aluminum powder with zeolite and activated alumina and is characterized by the structure shown in SEM micrograph (Fig. 12).

30. The material as in claim 20, wherein said material is made from the mixture of aluminum powder with zeolite and activated alumina and is characterized by the adsorption-desorption isotherms shown in Fig. 14, 16, 17.

31. The material as in claim 20, wherein said material is made from the mixture of aluminum powder with zeolite and activated alumina and is characterized by the dependence of the sorption pore volume of composite  $\text{NaA/Al/Al(OH)}$  on the ratio of zeolite powder/aluminum powder shown in Fig. 15.

32. The material as in claim 20, wherein said material is characterized by the dependence of its mechanical strength on the adsorbent dispersion and content shown in Fig. 18.

33. The material as in claims from 20 to 28, wherein the above-described procedures are performed a number of cycles during the material synthesis.

34. The material as in claim 33, wherein said material is characterized by the dependence of its mechanical strength on the aluminum transformation level (number of treatment cycles) for various powder-like adsorbents shown in Fig. 19.

35. A synthetic composite gas-and-fluid permeable material in the form of a solid with a porous-open structure of crystallite aggregates of aluminum hydroxide ( $\text{Al(OH)}_3$  or  $\text{AlOOH}$ ) or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) coupled by phase contacts, wherein said material is made with the specific surface from  $50$  to  $200\text{ m}^2/\text{g}$  and presents a layer having a thickness  $3$  to  $50$  of particle diameters of primary aluminum powder deposited on the whole or a fraction of a solid substrate surface of aluminum or other metal or nonmetal coated by an aluminum layer coupled to said substrate by crystallite aggregates of ( $\text{Al(OH)}_3$  or  $\text{AlOOH}$ ) hydroxide or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ), while the space between said crystallites presents pores having a diameter from  $4.5\text{ nm}$  to  $100\text{ }\mu\text{m}$  and said material is synthesized by the dissolution of aluminum in an aqueous solution having  $\text{pH}=7.5\text{-}11.5$  at the maximum temperature of  $100^{\circ}\text{C}$  (preferably from  $85$  to  $95^{\circ}\text{C}$ ) followed by the mass crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving disperse and solid aluminum.

36. The material as in claim 35, wherein said material additionally comprises separate aluminum particles surrounded by porous shells composed of crystallite aggregates of aluminum hydroxide ( $\text{Al(OH)}_3$  or  $\text{AlOOH}$ ) or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) and coupled by phase contacts in the form of crystallite aggregates having a similar structure.

37. The material as in claim 35, wherein a disperse aluminum layer is deposited onto the surface of said substrate by dipping, spraying or spreading, for example, from a volatile liquid slurry containing aluminum particles.

38. The material as in claim 35, wherein the dissolution of aluminum during the material synthesis is provided in the process of a heterogeneous chemical reaction of aluminum with an aqueous solution having pH=7.5-11.5.

39. The material as in claims from 35 to 38, wherein the dissolution of aluminum during the material synthesis is provided by means of the thermal treatment of the substrate having thereon a pre-deposited layer impregnated with an aqueous solution having pH=7.5-11.5 at the maximum temperature of 100°C for 2-3 hrs.

40. The material as in claim 35, wherein said material is additionally subjected to a thermal treatment at the temperature from 450° to 550°C until aluminum hydroxide is fully transformed into alumina.

41. The material as in claim 40, wherein said material when used as a layer on a solid aluminum substrate is characterized by a structure shown in SEM micrograph in Fig. 20.

42. The material as in claim 40, wherein said material when used as a layer on a solid aluminum substrate is characterized by adsorption-desorption isotherms shown in Fig. 21.

43. A synthetic composite gas-and-fluid permeable material in the form of a solid with a porous-open structure of crystallite aggregates of aluminum hydroxide ( $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$ ) or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) coupled by phase contacts, wherein said material is made with the specific surface from 50 to 200  $\text{m}^2/\text{g}$  and on the surface of one or a number of porous or non-porous, nonmetallic or metallic elements coupled by mechanical or phase contacts in the form of crystallite aggregates of hydroxide ( $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$ ) or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ), while the space between said crystallites presents pores having a diameter from 4.5 nm to 100  $\mu\text{m}$  and said material is synthesized by the dissolution of disperse aluminum in an aqueous solution having pH=7.5-11.5 at the maximum temperature of 100°C (preferably from 85 to 95°C) followed by the mass crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum and in the area of inter-particle contacts.

44. The material as in claim 43, wherein said material additionally comprises separate aluminum particles surrounded by porous shells composed of crystallite aggregates of aluminum hydroxide ( $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$ ) or alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) and coupled by phase contacts in the form of crystallite aggregates having a similar structure.

45. The material as in claim 43, wherein a disperse aluminum layer during the material synthesis is deposited on the whole or a fraction of the surface of a porous or non-porous, nonmetallic or metallic element, for example, in the shape of a pipe, sheet or bush etc. by dipping, spraying or spreading, for example, from a volatile liquid slurry containing aluminum particles.

46. The material as in claim 43, wherein the dissolution of aluminum during the material synthesis is provided in the process of a heterogeneous chemical reaction of aluminum with an aqueous solution having pH=7.5-11.5.

47. The material as in claims from 43 to 46, wherein the dissolution of aluminum during the material synthesis is provided by means of the thermal treatment of a substrate having thereon a pre-deposited layer impregnated with an aqueous solution having pH=7.5-11.5 at the maximum temperature of 100°C for 2-3 hrs.

48. The material as in claim 43, wherein said material is additionally subjected to a thermal treatment at the temperature from 450° to 550°C until aluminum hydroxide is fully transformed into alumina.

49. The material as in claims from 43 to 48, wherein the above-described procedures are performed a number of cycles during the material synthesis.

50. The material as in claims from 43 to 49, wherein during the material synthesis the porous or non-porous, nonmetallic or metallic elements with a pre-deposited porous layer are placed in the required succession into a divided or solid mold with further filling-in the spaces between said elements and between said elements and said mold with disperse aluminum or other disperse material coated by an aluminum layer or a slurry of disperse aluminum or other disperse material coated by an aluminum layer.

51. The material as in claim 50, wherein the dissolution of aluminum during the material synthesis is provided by impregnating the pre-formed elements with a pre-deposited porous layer and powder media with an aqueous solution having pH=7.5-11.5 in the volume of 0.01 to 0.95 of the total pore volume.

52. The material as in claims from 50 to 51, wherein the dissolution of aluminum during the material synthesis is provided during the thermal treatment of pre-formed elements and powder media impregnated with an aqueous solution having pH=7.5-11.5 at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

53. The material as in claims from 50 to 52, wherein an additional dissolution of aluminum during the material synthesis is provided by means of impregnating a cooled pre-formed porous body with an aqueous solution having pH=7.5-11.5 in the volume equal to the material total pore volume.

54. The material as in claims from 50 to 53, wherein an additional dissolution of aluminum during the material synthesis is provided by means of the thermal treatment of a pre-formed porous body impregnated with an aqueous solution having pH=7.5-11.5 at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

55. The material as in claims from 50 to 54, wherein said material is additionally subjected to a thermal treatment at the temperature from 450° to 550°C until aluminum hydroxide is fully transformed into alumina.

56. The material as in claims from 53 to 55, wherein the above-described procedures are performed a number of cycles during the material synthesis.

57. A synthetic composite gas-and-fluid permeable material in the form of a solid with a porous-open structure of alumina aggregates coupled by phase contacts, wherein said material is made with the specific surface up to 20 m<sup>2</sup>/g and presents a system of filament nanocrystals of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and a system of hollow spheres of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> coupled by phase contacts in the form of sintered crystallite aggregates of alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>), while the space between said crystallites presents pores having a diameter from 4.5 nm to 100  $\mu$ m and said material is synthesized by the dissolution of aluminum in an aqueous solution having pH=7.5-11.5 at the maximum temperature of 100°C (preferably from 85 to 95°C) followed by the mass crystallization of aluminum hydroxide crystallites from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts and subsequent baking at the temperature from 750 to 1450°C until aluminum hydroxide is fully transformed into corundum.

58. The material as in claim 57, wherein said material is synthesized from disperse aluminum or aluminum continuous/discontinuous fibers (wires).

59. The material as in claim 57, wherein the dissolution of aluminum during the material synthesis is provided in the process of a heterogeneous chemical reaction of aluminum with an aqueous solution having pH=7.5-11.5.

60. The material as in claims from 57 to 59, wherein the dissolution of aluminum during the material synthesis is provided by impregnating the pre-formed porous media with an aqueous solution having pH=7.5-11.5 in the volume of 0.01 to 0.95 of the pore volume of porous media.

61. The material as in claims from 57 to 60, wherein the dissolution of aluminum during the material synthesis is provided by means of the thermal treatment of the pre-formed powder impregnated with an aqueous solution having pH=7.5-11.5 at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

62. The material as in claim claims from 57 to 61, wherein an additional dissolution of aluminum during the material synthesis is provided by means of impregnating a cooled pre-formed porous body with an aqueous solution having pH=7.5-11.5 in the volume equal to the material pore volume.

63. The material as in claims from 57 to 62, wherein an additional dissolution of aluminum during the material synthesis is provided by means of the thermal treatment of a pre-formed porous body impregnated with an aqueous solution having pH=7.5-11.5 at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

64. The material as in claims from 57 to 63, wherein the above-described procedures are performed a number of cycles during the material synthesis.

65. The material as in claim 64, wherein said material is additionally subjected to a thermal treatment at the temperature from 750<sup>0</sup> to 1450<sup>0</sup>C until aluminum is fully vaporized and aluminum hydroxide and aluminum are fully transformed into corundum (alumina  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>).

66. The material as in claim 65, wherein said material is characterized by a microstructure shown in SEM micrograph (Fig. 26, 27).

67. The material as in claim 65, wherein said material is characterized by the dependence of adsorption-desorption isotherms on the baking temperature, shown in Fig. 28, a.

68. The material as in claim 65, wherein said material is characterized by the dependence of its specific surface and sorption pore volume on the baking temperature shown in Fig. 28, b.

69. A method of producing a synthetic composite gas-and-fluid permeable material including the formation of disperse aluminum, the dissolution of aluminum and further crystallization of aluminum hydroxide, wherein said dissolution of said aluminum is performed by means of impregnating the pre-formed powder with an aqueous solution having pH=7.5-11.5 in the volume of 0.01 to 0.95 of the powder media pore volume, while the subsequent mass crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts is provided by keeping in the air at the maximum temperature of 100°C (preferably from 85 to 95<sup>0</sup>C) for 1.5-2 hrs until water is fully vaporized.

70. The method as in claim 69, wherein an additional dissolution of aluminum during the material synthesis is provided by means of the thermal treatment of a cooled pre-formed porous body impregnated with an aqueous solution having pH=7.5-11.5 at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

71. The method as in claim 69, wherein said material is additionally subjected to a thermal treatment at the temperature from 450° to 550°C until aluminum hydroxide is fully transformed into alumina.

72. The method as in claims from 69 to 71, wherein the above-described procedures are performed a number of cycles.

73. The method of producing a synthetic composite gas-and-fluid permeable material including mixing the insoluble or slow soluble compounds in the form of metallic organic and/or inorganic, non-porous and porous disperse particles of various configurations and/or continuous fibers (threads) and disperse aluminum or other disperse material coated by an aluminum layer, the formation of said mixture, the dissolution of aluminum and the subsequent crystallization of aluminum hydroxide, wherein the dissolution of aluminum is performed by means of impregnating a pre-formed mixture with an aqueous solution having pH=7.5-11.5 in the volume of 0.01 to 0.95 of said mixture pore volume, while said subsequent mass crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts is provided by keeping in the air at the maximum temperature of 100°C (preferably from 85 to 95°C) for 1.5-2 hrs until water is fully vaporized.

74. The method as in claim 73, wherein an additional dissolution of aluminum during the material synthesis is provided by means of the thermal treatment of a cooled pre-formed porous body impregnated with an aqueous solution having pH=7.5-11.5 in the volume equal to the material pore volume.

75. The method as in claims 73 or 74, wherein an additional dissolution of aluminum during the material synthesis is provided by means of the thermal treatment of a cooled pre-formed porous body impregnated with an aqueous solution having pH=7.5-11.5 at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

76. The method as in from 73 to 75, wherein said material is additionally subjected to a thermal treatment at the temperature from 450° to 550°C until aluminum hydroxide is fully transformed into alumina.

77. The method as in claims from 73 to 76, wherein the above-described procedures are performed a number of cycles.

78. The method of producing a synthetic composite gas-and-fluid permeable material including the preparation of a slurry of aluminum powder in a carrier, preferably a volatile one, coating a fraction or the whole surface of a substrate with said slurry, drying a pre-deposited layer, the dissolution of aluminum and the subsequent crystallization of aluminum hydroxide, wherein the dissolution of aluminum is performed by impregnating the substrate and the pre-deposited layer with an aqueous solution having pH=7.5-11.5 in the volume of 0.01 to 0.95 of the total pore volume, while the subsequent crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts is provided by keeping in the air at the maximum temperature of 100°C (preferably from 85 to 95°C) for 1.5-2 hrs until water is fully vaporized.

79. The method as in claim 78, wherein the deposition of a disperse aluminum layer onto the surface of a solid substrate is preferably provided by means of dipping, spraying or spreading.

80. The method as in claim 78, wherein a substrate is made in the form of a single or a number of porous or nonporous nonmetallic or metallic elements.



81. The method as in claim 80, wherein a substrate is made in the form of a single or a number of winding bodies.

82. The method as in claim 81, wherein before application of a slurry a winding body is pressed out to achieve pre-defined dimensions.

83. The method as in claim 81, wherein a winding body with a pre-deposited porous layer is pressed out to achieve pre-defined dimensions.

84. The method as in claims from 78 to 83, wherein one or a number of said porous and/or non-porous elements with a pre-deposited porous layer are placed into a divided or solid mold and the spaces between said elements and said mold are filled with disperse aluminum or other disperse material coated by an aluminum layer or a slurry of disperse aluminum.

85. The method as in claim 84, wherein the dissolution of aluminum is performed by means of impregnating a substrate with a pre-deposited layer with an aqueous solution having  $\text{pH}=7.5-11.5$  in the volume of 0.01 to 0.95 of the total pore volume and the subsequent crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts is provided by keeping in the air at the maximum temperature of  $100^{\circ}\text{C}$  (preferably from  $85$  to  $95^{\circ}\text{C}$ ) for 1.5-2 hrs until water is fully vaporized.

86. The method as in claims from 78 to 85, wherein an additional dissolution of aluminum is provided by means of impregnating a cooled pre-formed porous body with an aqueous solution having  $\text{pH}=7.5-11.5$  in the volume equal to the material total pore volume.

87. The method as in claim from 78 to 86, wherein an additional dissolution of aluminum is provided by means of the thermal treatment of a cooled pre-formed porous body impregnated with an aqueous solution having  $\text{pH}=7.5-11.5$  at the temperature from  $85$  to  $95^{\circ}\text{C}$  for 1.5-2 hrs until water is fully vaporized.

88. The method as in claims from 78 to 87, wherein said porous body in a mold or after extraction from said mold is additionally subjected to a thermal treatment at the temperature from  $450^{\circ}$  to  $550^{\circ}\text{C}$  until aluminum hydroxide is fully transformed into alumina.

89. The method as in claims from 78 to 88, wherein the above-described procedures are performed a number of cycles.

90. The method as in claims from 78 to 89, wherein an additional thermal treatment of a porous material is performed at the temperature from  $750^{\circ}$  to  $1450^{\circ}\text{C}$  until aluminum is vaporized and aluminum hydroxide and aluminum are fully transformed into corundum (alumina  $\alpha\text{-Al}_2\text{O}_3$ ).

91. A method of producing a synthetic composite gas-and-fluid permeable material including the formation of aluminum powder, the dissolution of aluminum and the subsequent crystallization of aluminum hydroxide crystallites, wherein the dissolution of aluminum is performed by means of impregnating a pre-formed powder with an aqueous solution having  $\text{pH}=7.5-11.5$  in the volume of 0.01 to 0.95 of the pore volume of powder media, while the subsequent crystallization of aluminum hydroxide from a supersaturated solution of monomer aluminum hydroxocomplexes onto the surface of dissolving aluminum particles and in the area of inter-particle contacts is provided by keeping in the air at the maximum temperature of  $100^{\circ}\text{C}$  (preferably from  $85$  to  $95^{\circ}\text{C}$ ) until water is fully vaporized followed by baking at the temperature from  $750$  to  $1450^{\circ}\text{C}$  to vaporize of aluminum until aluminum hydroxide is fully transformed into corundum.

92. The method as in claim 91, wherein an additional dissolution of aluminum is performed by means of the thermal treatment of a cooled pre-formed porous body impregnated with an aqueous solution having pH=7.5-11.5 in the volume equal to the material pore volume at the temperature from 85 to 95°C for 1.5-2 hrs until water is fully vaporized.

93. The method as in claim 92, wherein the material is additionally subjected to baking at the temperature from 450° to 550°C for 1 hr until aluminum hydroxide is fully transformed into alumina.

94. The method as in claims from 91 to 93, wherein the above-described procedures are performed a number of cycles.

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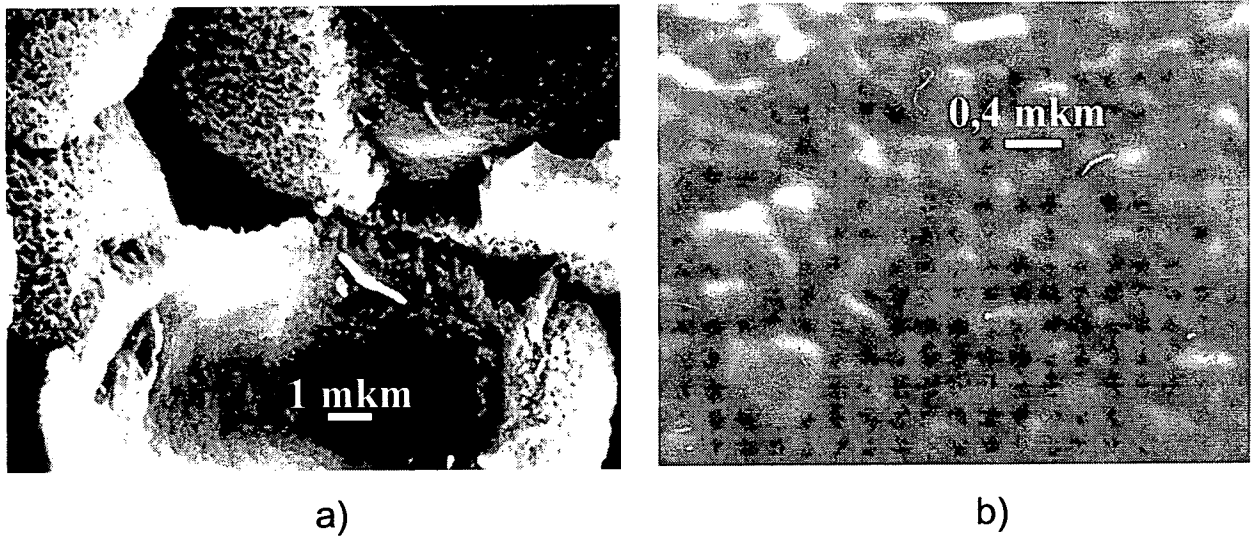


Fig. 1.

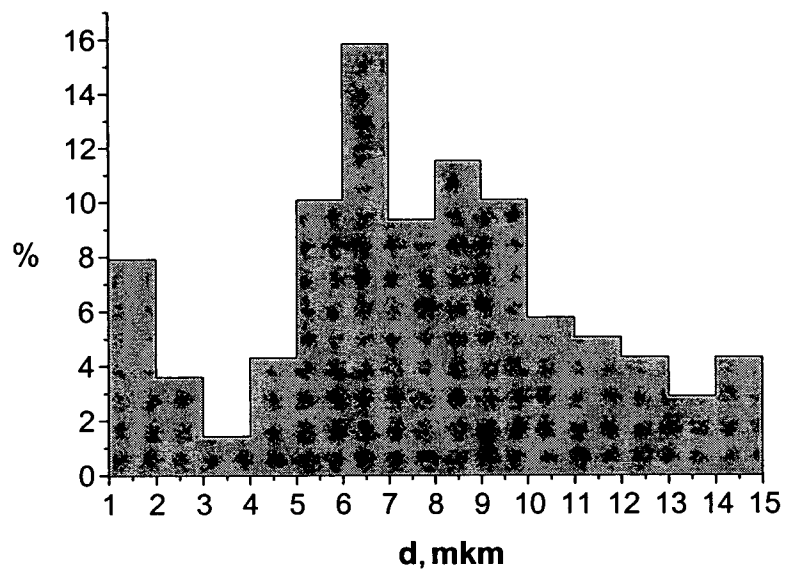


Fig. 2.

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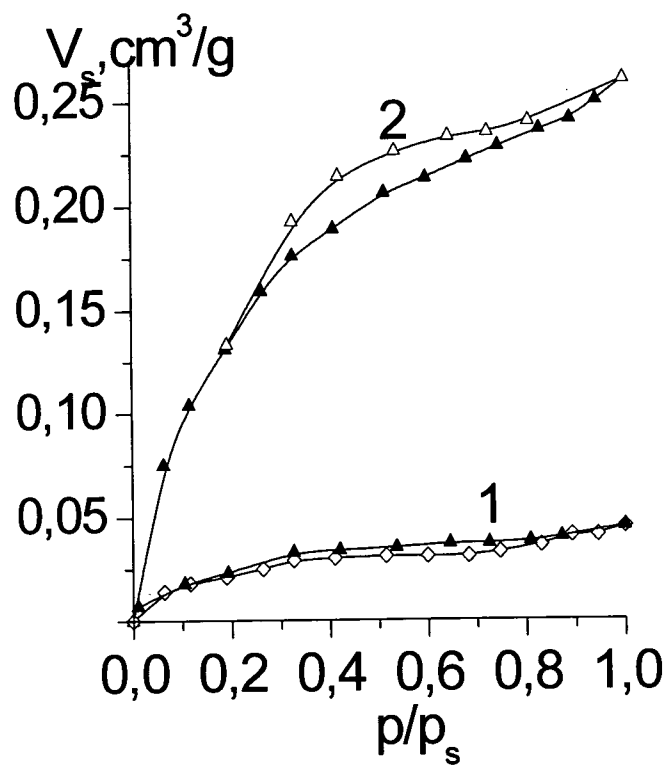


Fig. 3.

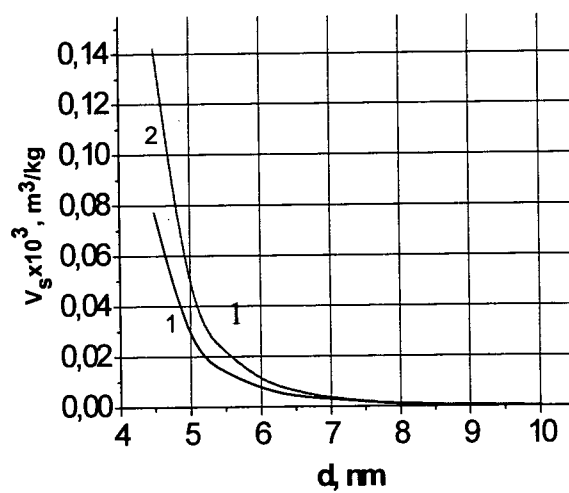


Fig. 4.

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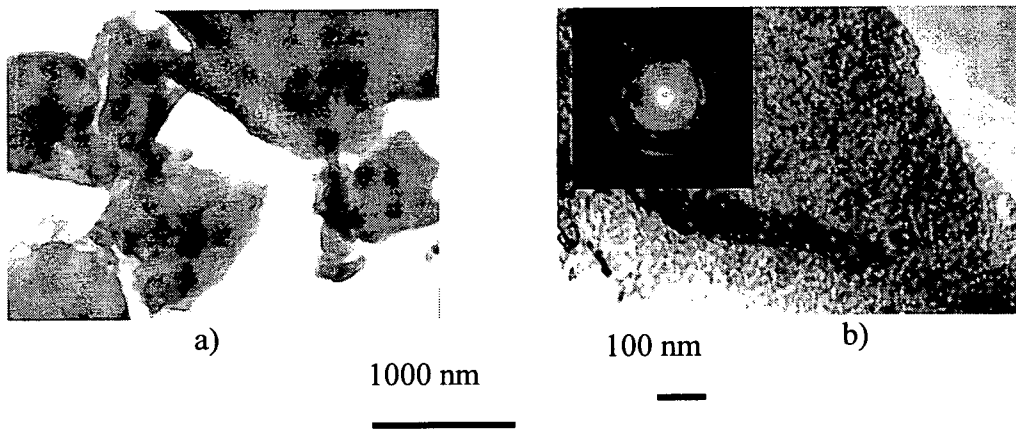


Fig. 5.

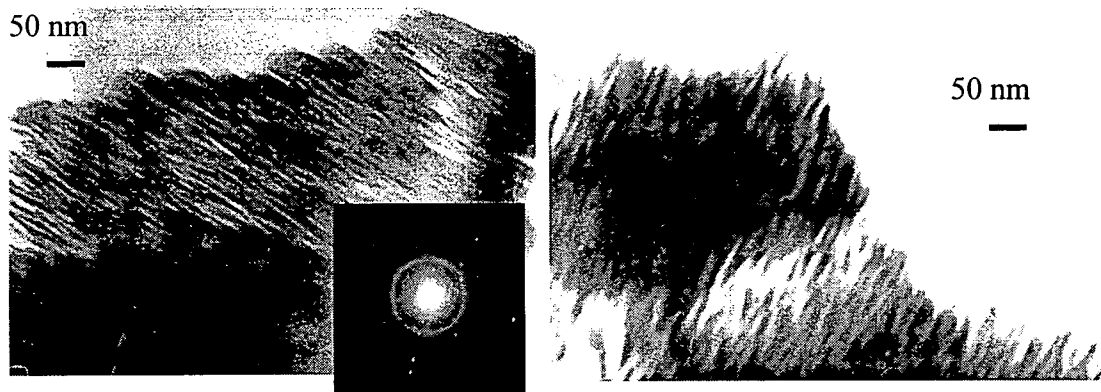


Fig. 6.

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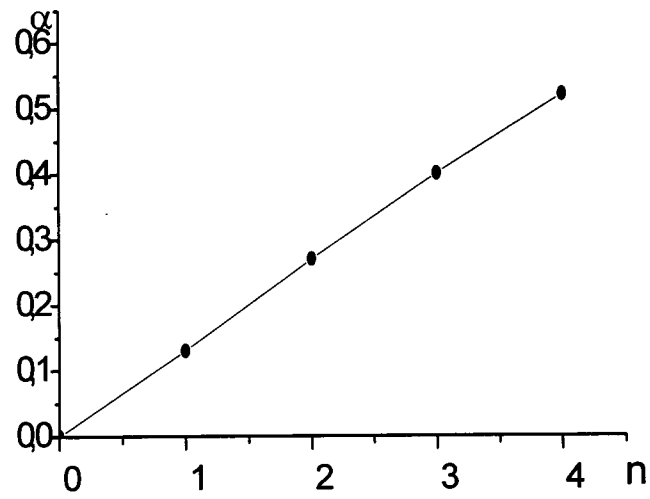


Fig. 7.

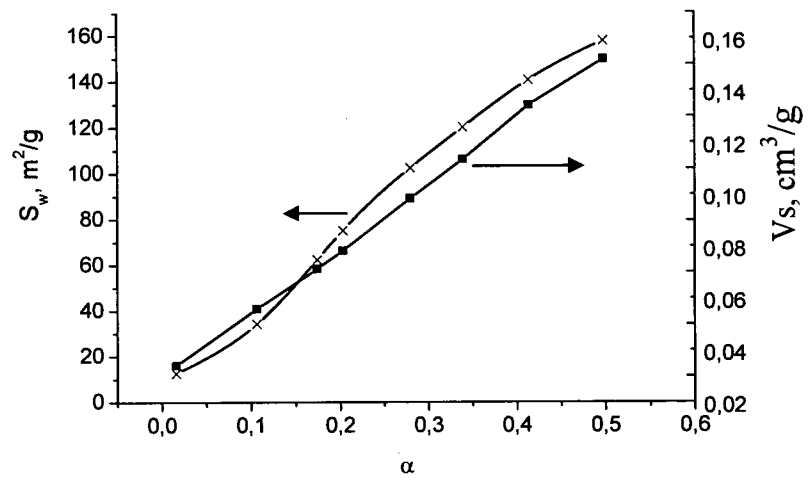
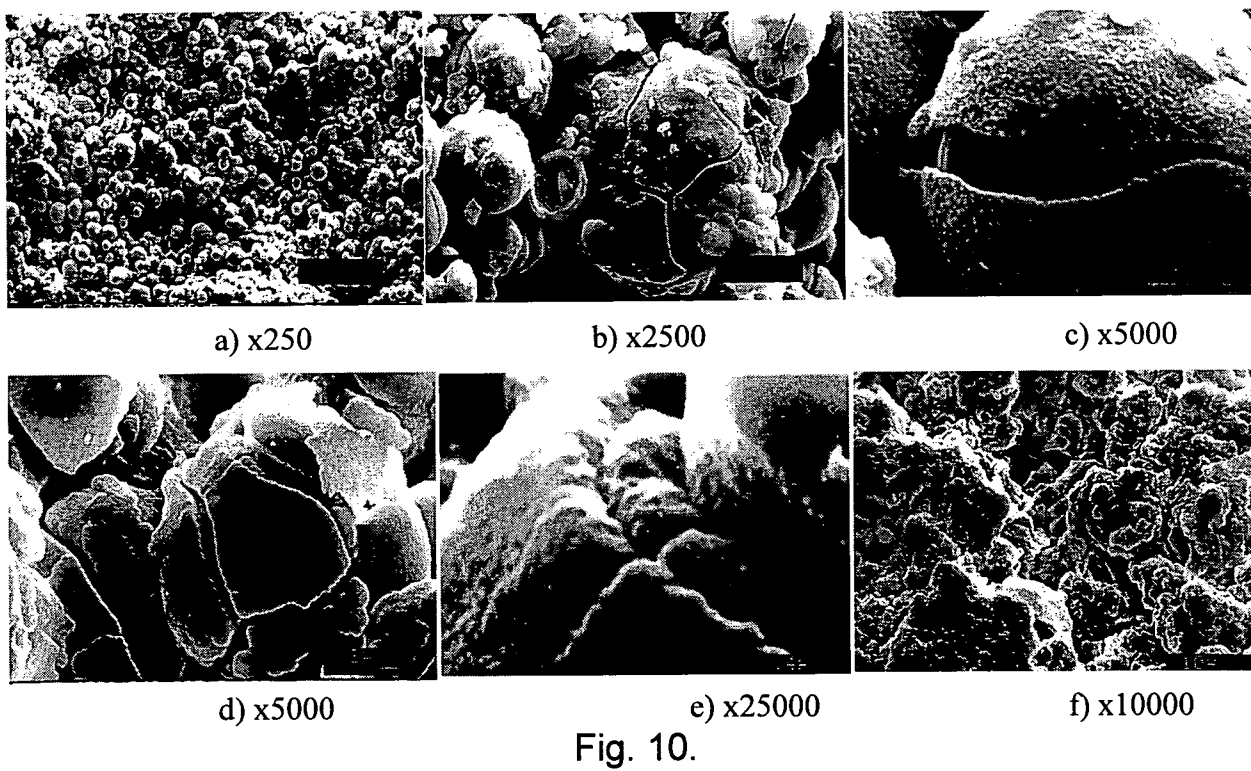
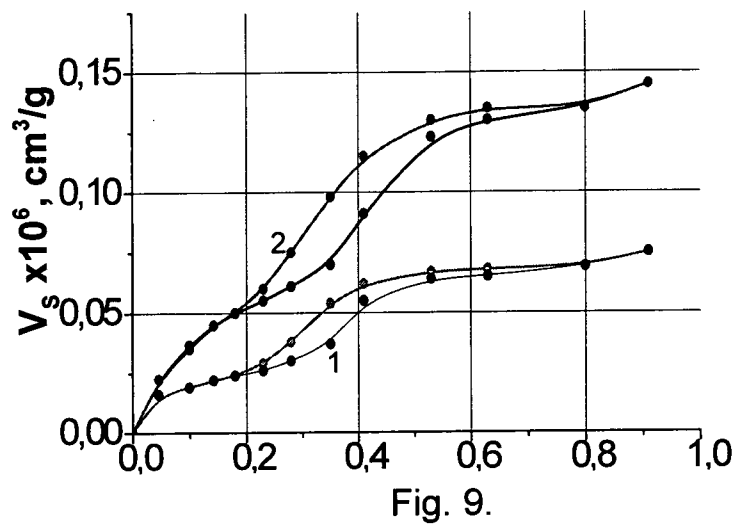


Fig. 8.

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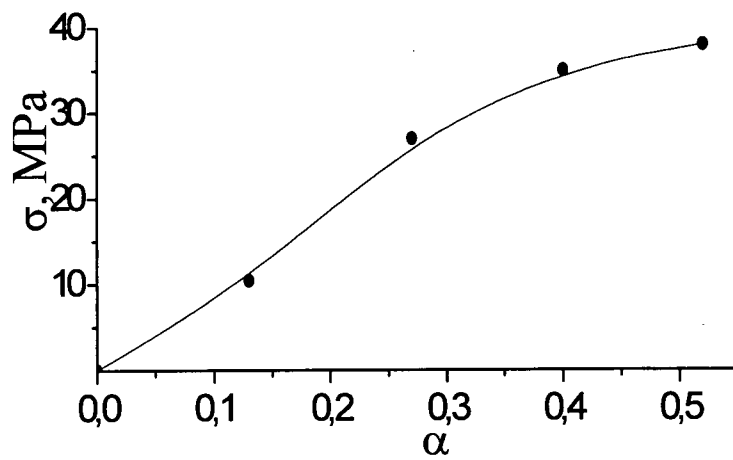
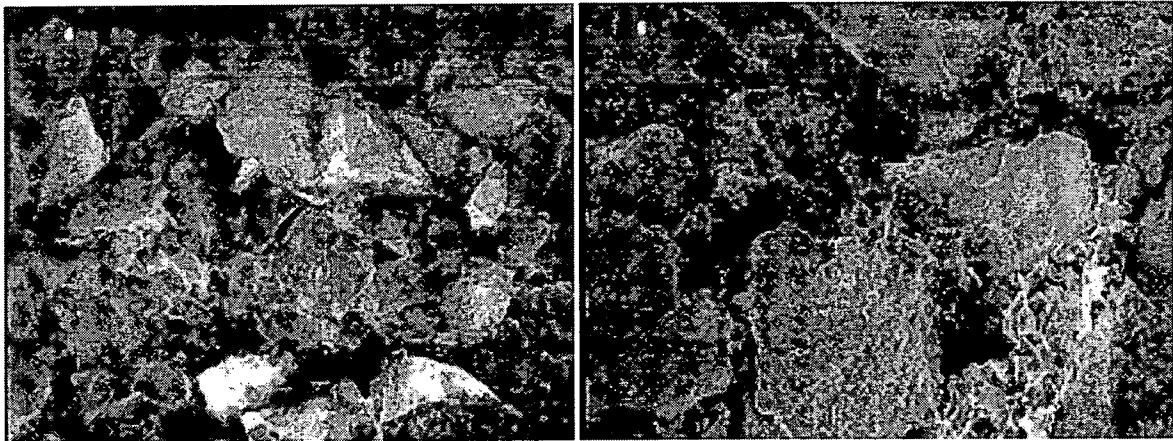


Fig. 11.



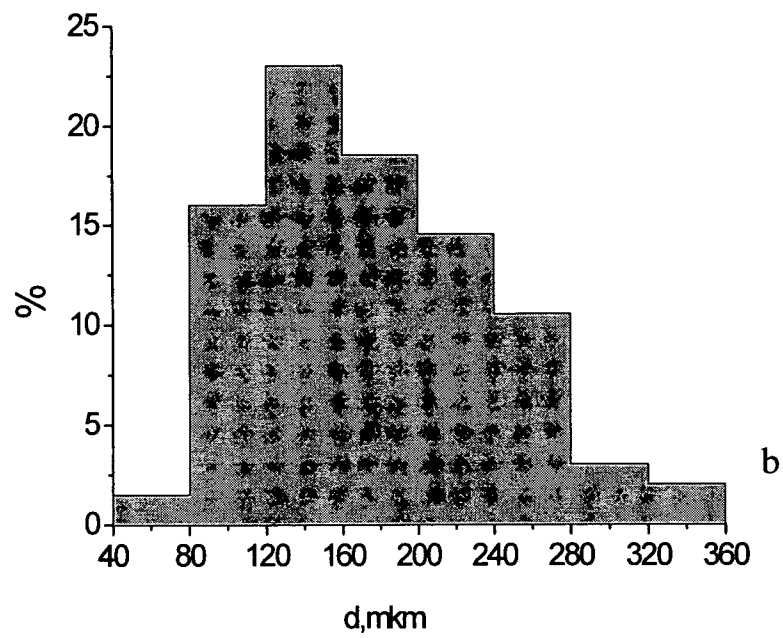
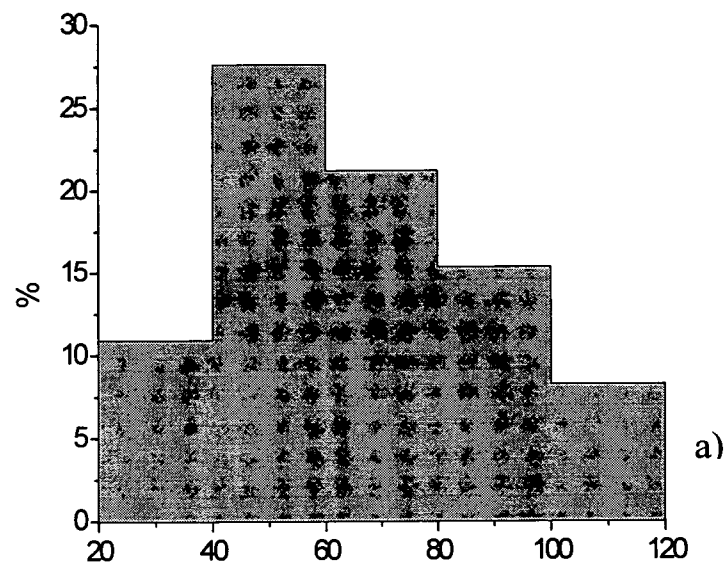
a) x25

b) x100

Fig. 12.



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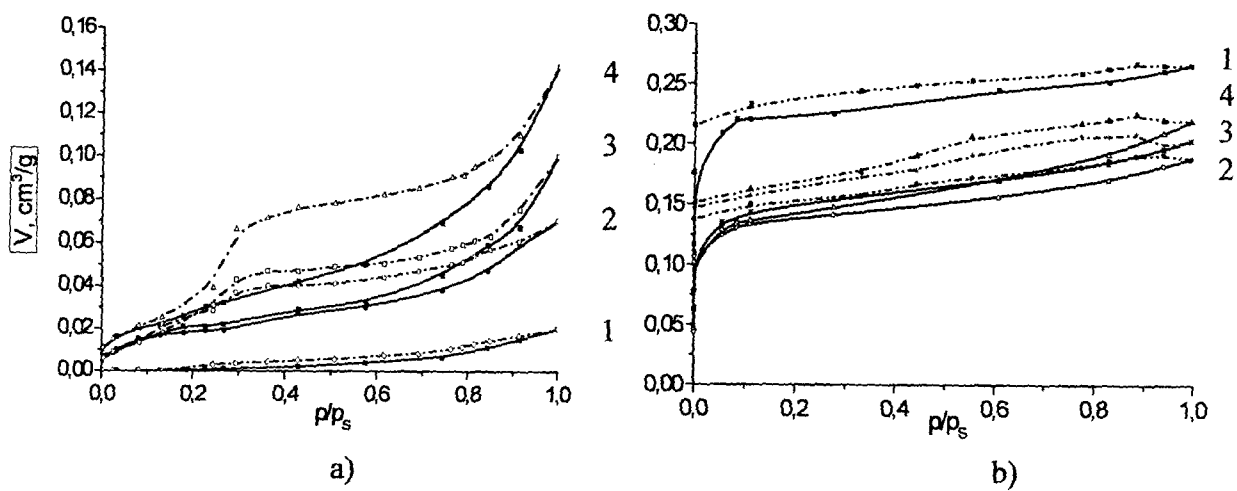


Fig. 14.

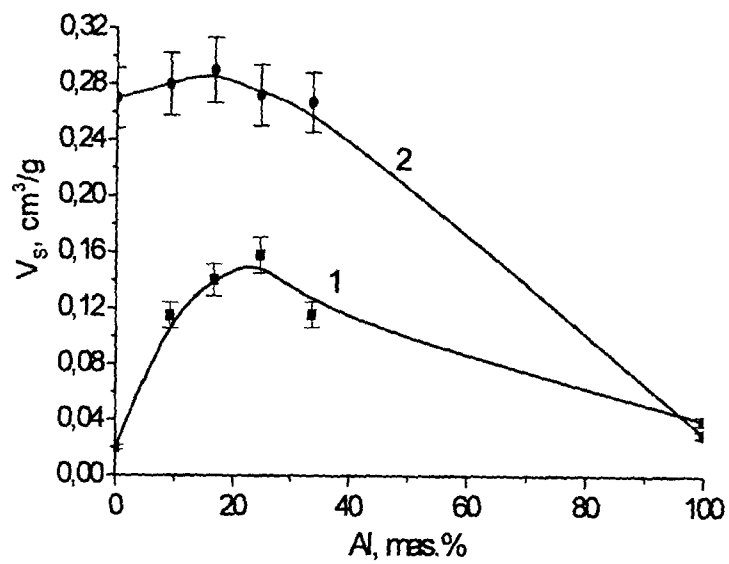


Fig. 15.

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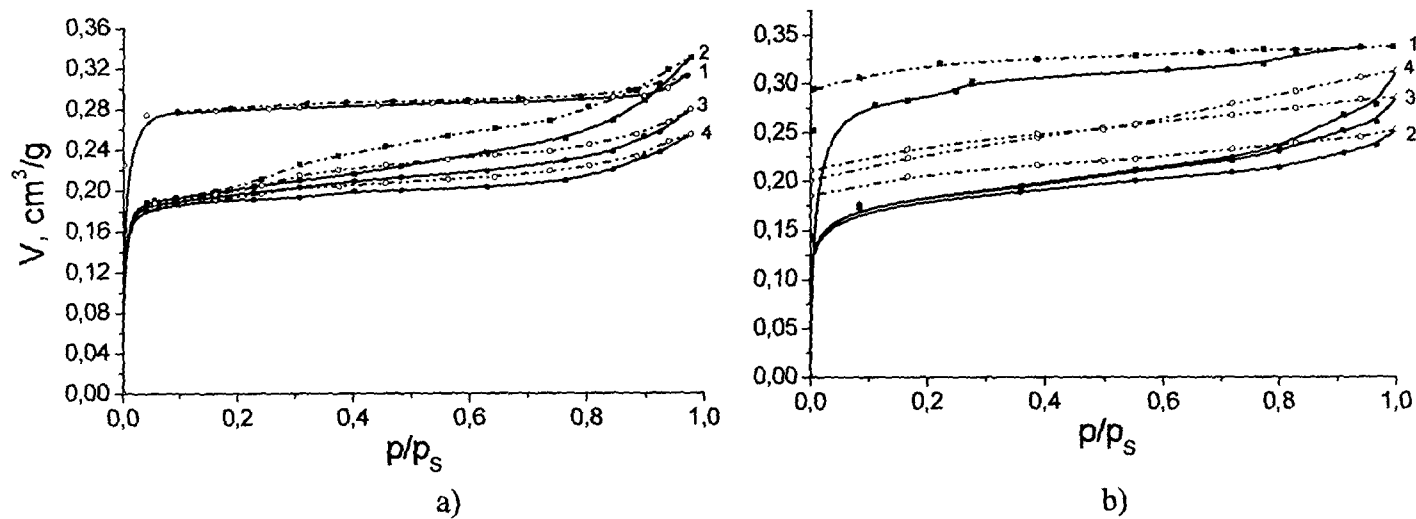


Fig. 16.

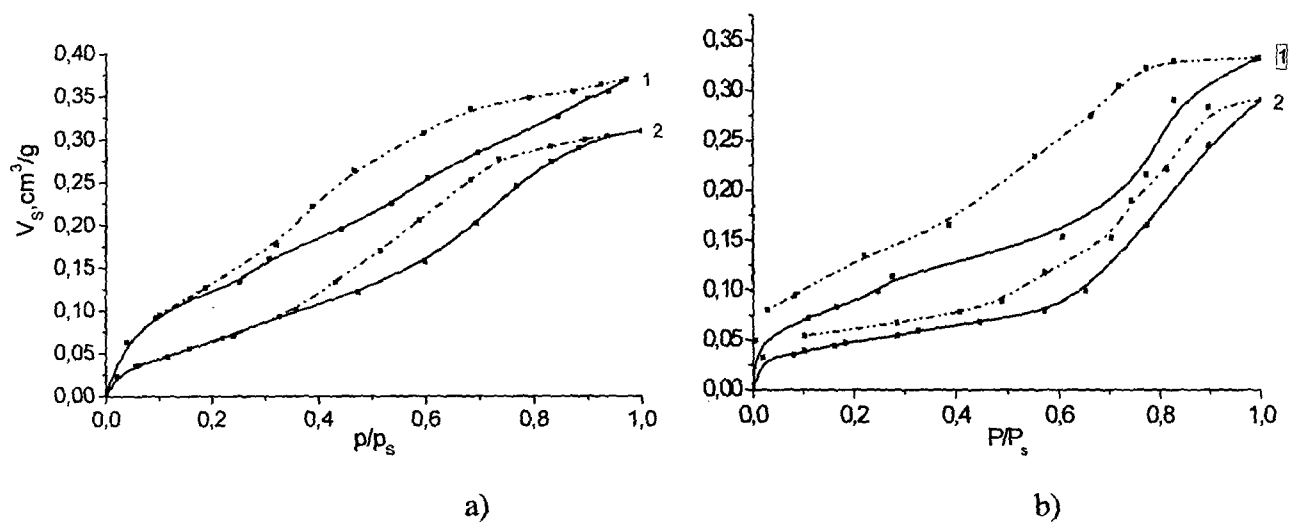


Fig. 17.

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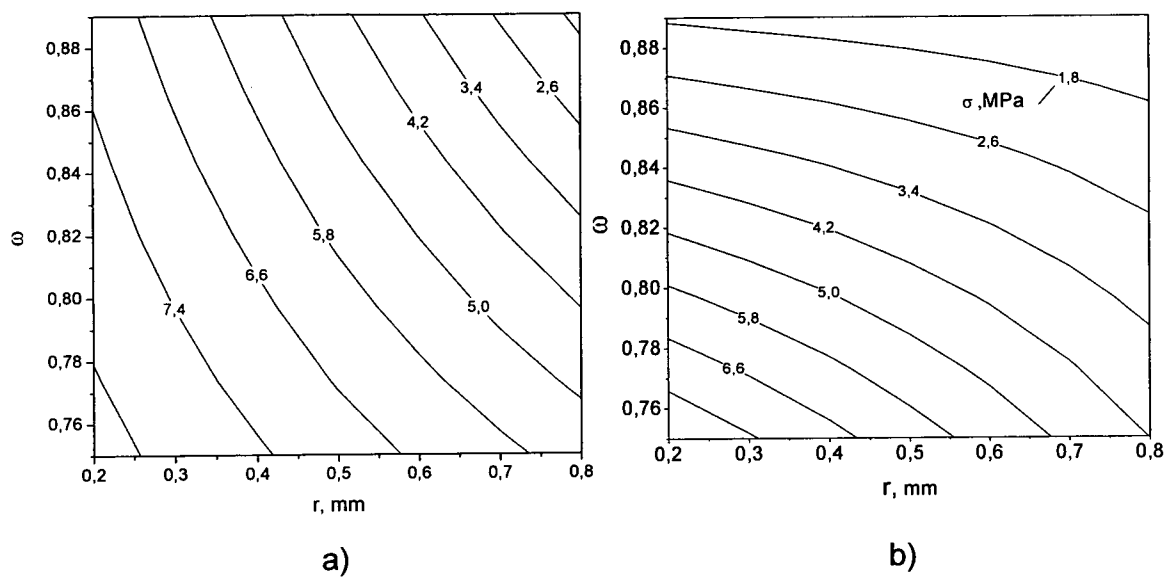


Fig. 18.

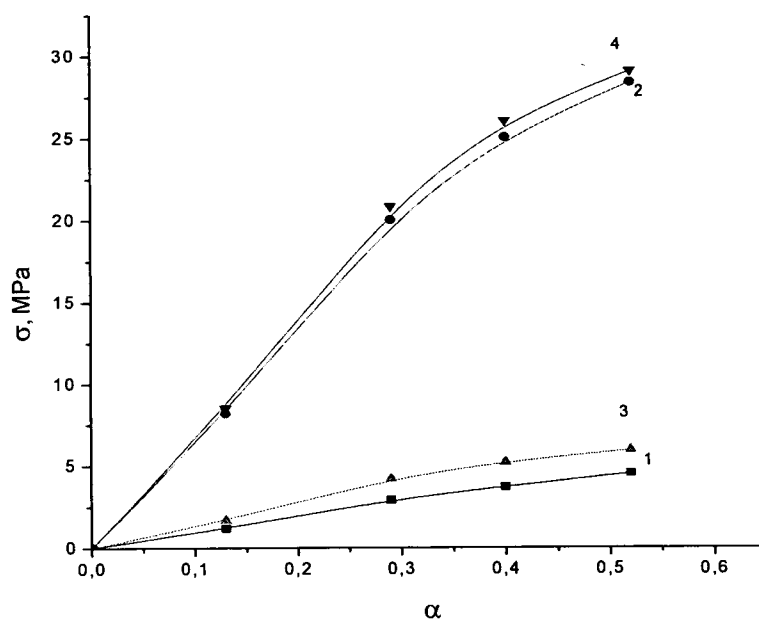


Fig. 19.

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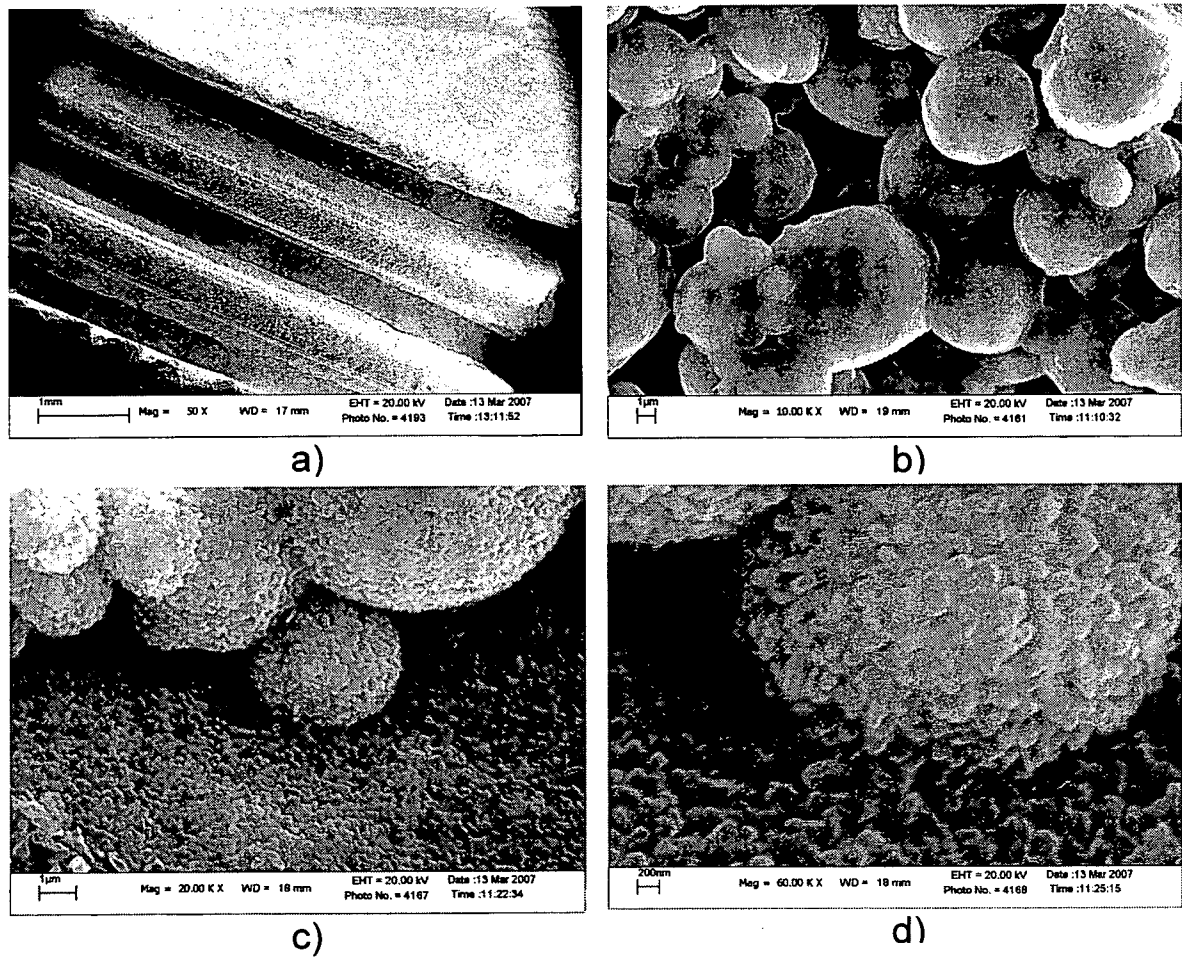


Fig. 20.

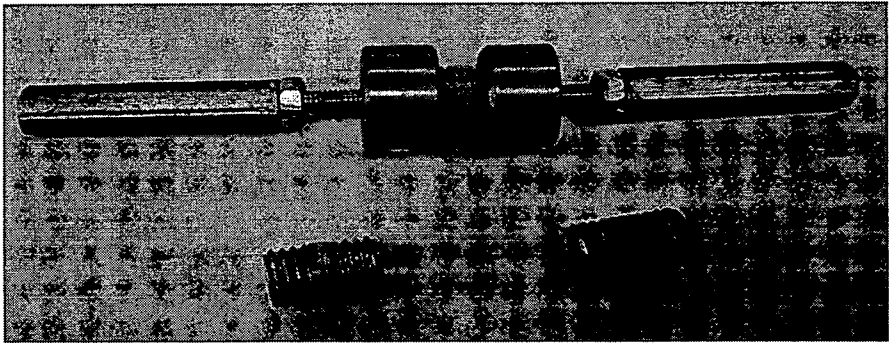


Fig. 21.

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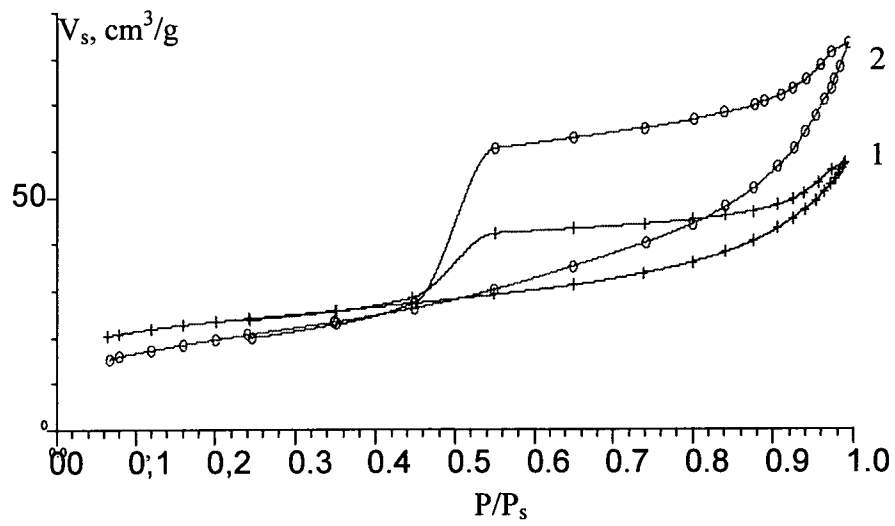


Fig. 22.

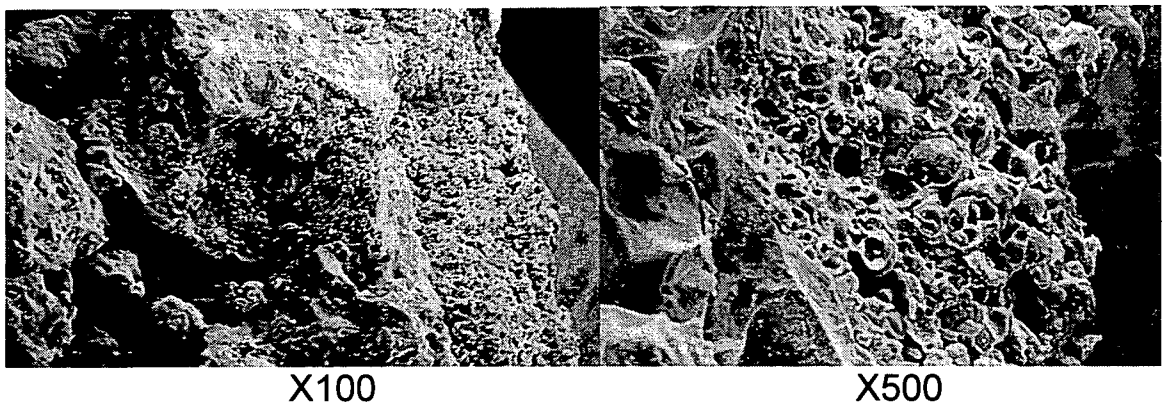
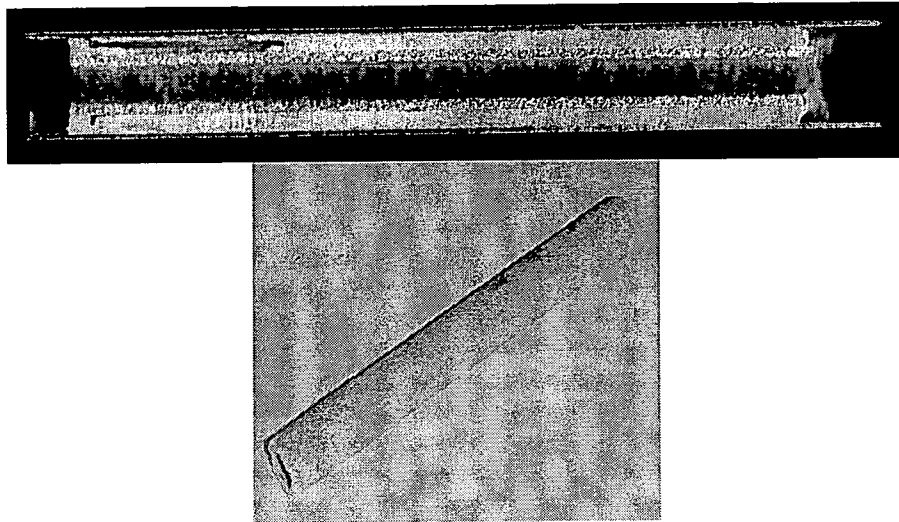


Fig. 23.

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a)



b)

Fig. 24.

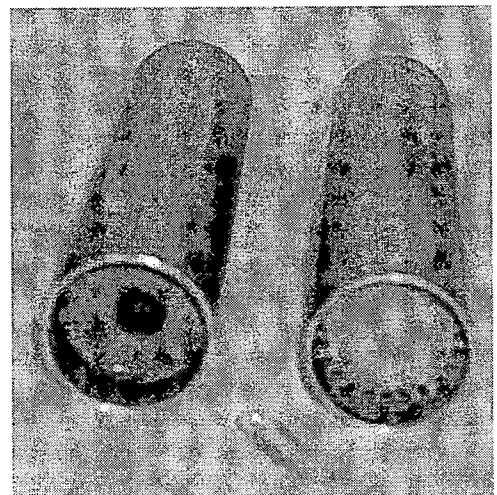
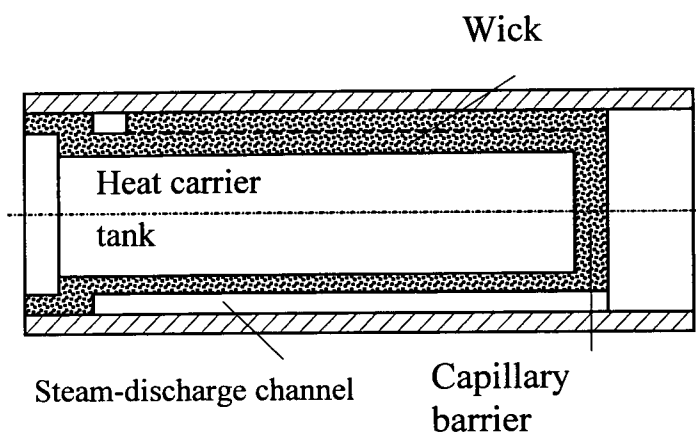


Fig. 25.

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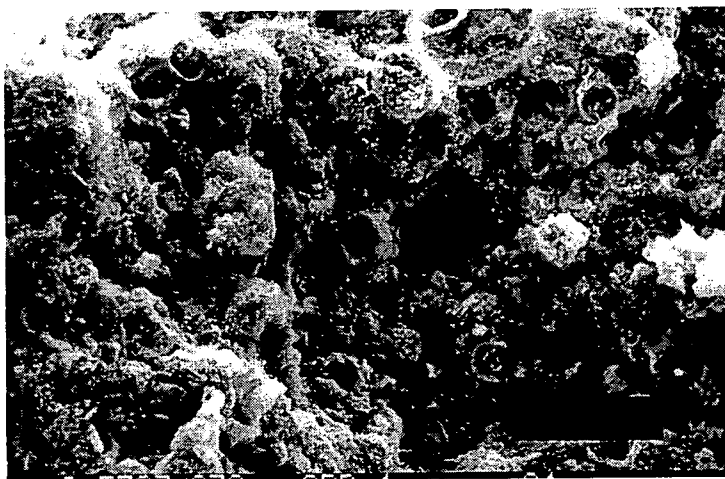


Fig. 26.

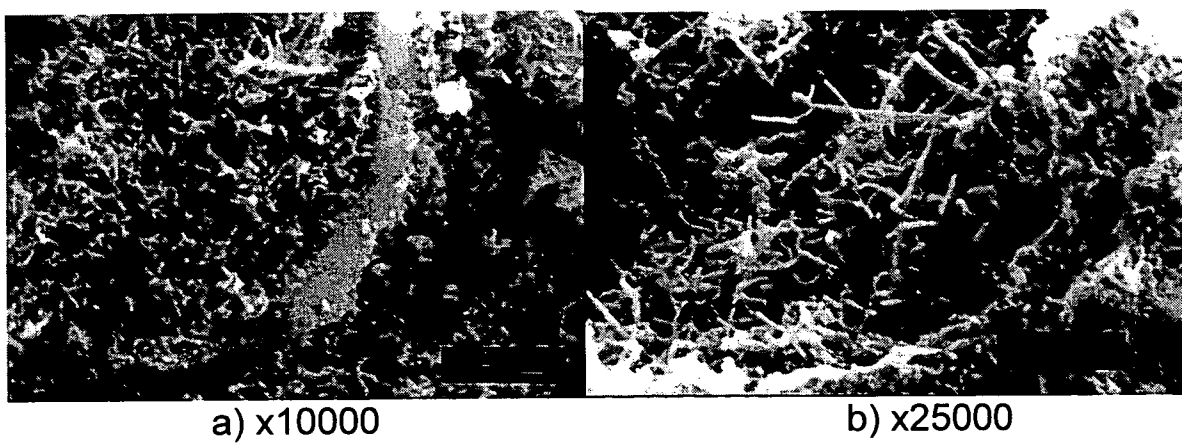


Fig. 27.



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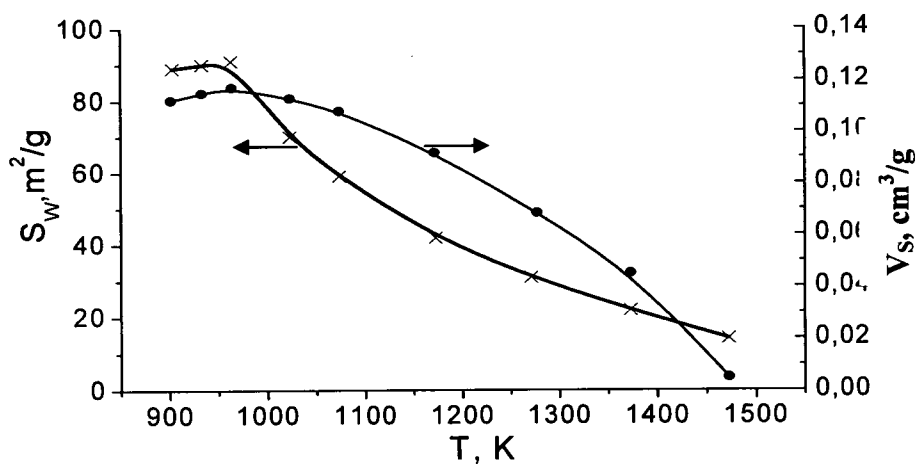
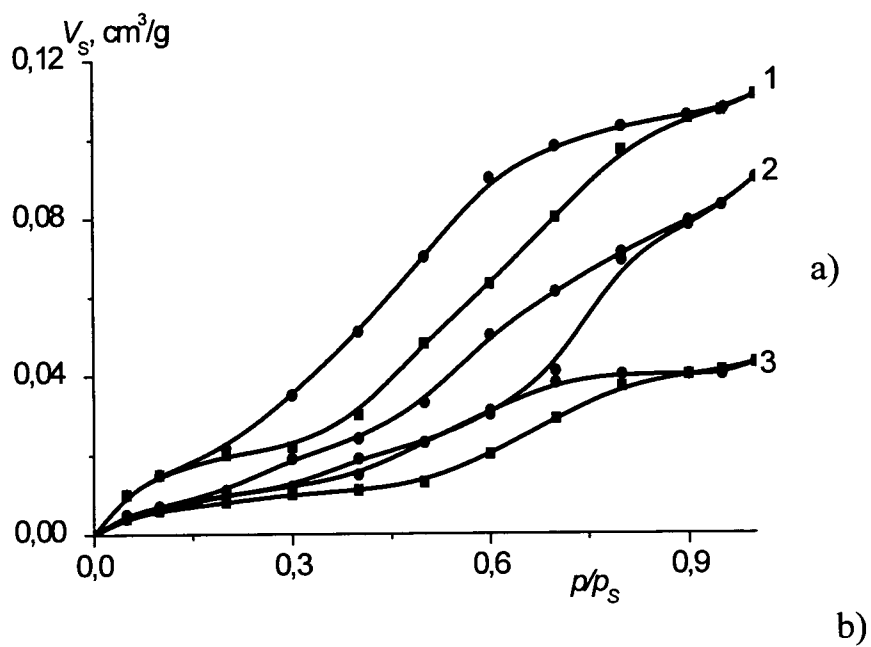


Fig. 28.

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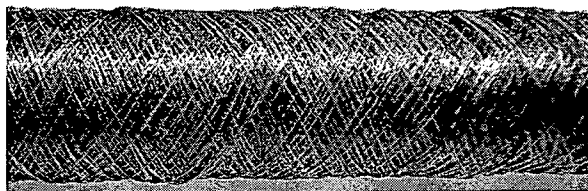


Fig.29

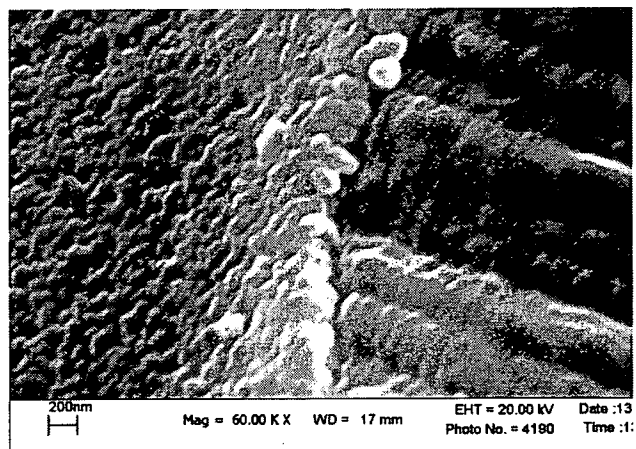


Fig.30

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/BY2008/000003

## A. CLASSIFICATION OF SUBJECT MATTER

INV. B22F1/00 B01J21/04 B22F1/02 C01F7/02 C01F7/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B22F B01J C01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, INSPEC, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 972 748 A (JAPAN ENERGY CORP [JP]) 19 January 2000 (2000-01-19) paragraphs [0010], [0012], [0017], [0022], [0028], [0036], [0040], [0041]; example 1	1-56, 69-90
X	EP 1 894 625 A (JAPAN ENERGY CORP [JP]) 5 March 2008 (2008-03-05) paragraphs [0014], [0018] - [0022], [0028] - [0032], [0038] - [0040], [0053] - [0055]; table 1	1-56, 69-90

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*G\* document member of the same patent family

Date of the actual completion of the international search

23 January 2009

Date of mailing of the international search report

08/05/2009

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
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Juhart, Matjaz

## INTERNATIONAL SEARCH REPORT

International application No

PCT/BY2008/000003

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	TIKHOV S F ET AL: "Physicochemical Principles of the Synthesis of Porous Composite Materials through the Hydrothermal Oxidation of Aluminum Powder" KINETICS AND CATALYSIS, KLUWER ACADEMIC PUBLISHERS, BO, vol. 46, no. 5, 1 September 2005 (2005-09-01), pages 641-659, XP019298418 ISSN: 1608-3210 abstract; figures 1,12,14	1-56
A	RU 2 131 774 C1 (BORESKOVA INST KATALIZA SIBIR) 20 June 1999 (1999-06-20) cited in the application claims 1-8	1-56, 69-90
A	TIKHOV S F ET AL: "Hydrothermal synthesis of mechanically strong porous composites of MeO x/Al <sub>2</sub> O <sub>3</sub> /Al type" MATERIALS RESEARCH SOCIETY SYMPOSIUM PROCEEDINGS, MATERIALS RESEARCH SOCIETY, PITTSBURG, PA, vol. 878, 1 January 2005 (2005-01-01), pages 105-110, XP009111062 ISSN: 0272-9172 abstract; figure 1; tables 1-3	1-56, 69-90
A	KUZ'MIN A E ET AL: "Fischer-Tropsch Catalysts Based on Zr-Fe Intermetallides Encapsulated in an Al <sub>2</sub> O <sub>3</sub> /Al Matrix" KINETICS AND CATALYSIS, KLUWER ACADEMIC PUBLISHERS, BO, vol. 46, no. 5, 1 September 2005 (2005-09-01), pages 743-751, XP019298429 ISSN: 1608-3210 page 743, right-hand column - page 744, left-hand column; figures 6,7; tables 1,2	1-56, 69-90

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/BY2008/000003

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search reportcovers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

see additional sheet(s)

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/SA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-56,69-90

Porous ceramic materials comprising aggregates of aluminium hydroxide or "gamma -Al<sub>2</sub>O<sub>3</sub>" and having the specific surface between 50 and 200 m<sup>2</sup>/g, and corresponding production methods.

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2. claims: 57-68,91-94

Porous ceramic material comprising aggregates of corundum " alfa-Al<sub>2</sub>O<sub>3</sub>" and having the specific surface up to 20 m<sup>2</sup>/g, and a method of its production.

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No

PCT/BY2008/000003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0972748	A	19-01-2000	CN 1428298 A	09-07-2003
			CN 1255905 A	07-06-2000
			ID 24852 A	24-08-1999
			WO 9938802 A1	05-08-1999
			US 6429172 B1	06-08-2002
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EP 1894625	A	05-03-2008	NONE	
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RU 2131774	C1	20-06-1999	NONE	
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