Journal of International Scientific Publications: Materials, Methods and Technologies

Volume 8, ISSN 1314-7269 (Online), Published at: http://www.scientific-publications.net

SOME ISSUES ON ULTRAFINE α-ALUMINA POWDERS FABRICATED BY LOW TEMPERATURE SYNTHESIS

Tinatin V. Kuchukhidze, Vakhtang G. Gabunia, Zurab V. Fachulia, Natia T. Jalagonia, Roin V.Chedia

Laboratory Chemical Technology, I. Vekua Sukhumi Institute of Physics and Technology,

7 Mindeli Str, 0186, Tbilisi, Georgia

Abstract

Thermal treatment (>1200^oC) of unstable intermediate phases of aluminum hydroxides and aluminum oxides inspires formation of thermodynamically stable α-Al_2O_3 which is widely applied in the production of ceramics with different functional purposes. Low-temperature phase transformation and obtaining of α-Al_2O_3 nanopowders is possible , if in the reaction mixture is added a small amount of up to 5% α-Al_2O_3 (during decomposition, hydrolysis, drying-heating and annealing of precursors). Modified polymer-precursor and solution combustion techniques were used for obtaining α-alumina. Aluminum nitrates, aluminum alkoxydes, oxidants and bifunctional compounds for producing organic-inorganic gels were used as initial precursors. Organic-inorganic gels were obtained by homogenization of aluminum and organic compounds within the range of 80-200°C and by carbonization of the obtained mass within the temperature range of 300-800°C. The addition of 3-5% α–Al_2O_3 seeds in the initial reactive mixture decreases γ→α phase transformation temperature (1200°C) to 1020-1080°C. It was established, that during the interaction between aluminum nitrates and urea, adding of aluminum caused obtaining of amorphous aluminum oxide, annealing of which for 2h at 800°C on the open air gave α-Al_2O_3. There were studied possibilities of obtaining nano-phase powders by low-temperature (20-90^oC) corrosion of aluminum activated with mercury. Subsequent annealing of the obtained Al2O3·nH_2O amorphous powder at 1000-1100^oC resulted in the formation of α-Al_2O_3 fibers. XRD analysis showed that Al_2O_3 fibers contained particles with primary crystallites of 10-30 nm sizes.

Key words: *α-Alumina, Seeding, Combustion, Phase transformation*

INTODRUCTION

Nanopowders have a high application potential in obtaining electronic, electrotechnical ceramic bio-compatible materials, catalysts, adsorbents, membranes, filters, synthetic jewelry stones, single crystals and others. Physicomechanical properties of ceramic materials are depended on obtaining nanopowders and their consolidation methods. Improvement of the properties of ceramic materials is possible by formation of nanocrystalline structure [1-3]. Ceramic material with coarse-crystalline structure is characterized by fragility, ability of generating cracks, small endurance towards erosive and abrasive influence. Traditional methods of improving ceramic materials properties practically exhausted all resources. One of the real ways for developing this field is applying nanotechnologies, modifying nano-powders with opposite material of coarse-grained structure formation, their consolidation in finished product with preserving particles nano-sizes.

Physicomechanical properties of nanostructural ceramic products several times surpass the parameters of the product obtained by traditional methods that is stipulated by structural-morphological peculiarities of nan-systems, in particular, by existence of excessive surface energy, those are successfully applied in obtaining unique ceramic composites. Specific properties of separate particles are revealed when their size is less than 100 nanometer. In this case, number of atoms on the surface and in the volume of a particle are equal. For example, cube with 5nm facet consists of 1000 atoms, from which 40% are located on the nanoparticle surface. For comparison, particle with 0,1μm size consists of 10^7atoms or single cell, from which only 1% is located on the surface [4]. By reducing nanoparticle sizes the ratio of surface/volume increases. In one mole of these compounds nanopowders surface reaches several km^2, and their bulk density is ~0,1g/cm^3. For this reason, share of the surface energy sharply increases in the total energy of the whole particles. Dependence of surface and volume on the particle size is perfectly demonstrated in the Ref. [5]: 50 kg quartz of cube shape, length of its facet reaches 27 cm, and surface area - 0.44 m^2. Dividing this specimen into cubes of 1 mm^3 volume causes increase of the surface area up to 120 m^2, and in case of dividing specimen into 5 nm^3 volume cubes surface area increases up to 2 km^2. Due to the above mentioned, structural-morphological construction and properties of nanoparticles are sharply different from coarse-crystalline particles of the same material. Accordingly performance characteristics of nanostructural ceramic products, obtained from these powders are significantly

improved, in comparison with the products received by the traditional methods. At the same time, consolidation temperature of nanoparticles is several hundred degrees lower in comparison with coarse-grained powders, which contributes to the formation of nanostructure of the product [6,7].

Ceramic obtained on the base of aluminum oxide has wide application range, because it has unique properties, for example, high density, wear-resistance, dielectric characteristics, and exploitation ability at high temperatures and in corrosive atmosphere. they are widely used in electrotechnics (insulator), electron systems (multiepitaxial layers grown on sapphire single crystals), aviation and aerospace technologies, in medicine (bio-compatible ceramics), laser technology (transparent glass) and others. There are lots of methods for obtaining ultra-dispersive Al_2O_3, including sol-gel process, precipitation, chemical decomposition, plasma-chemical, electro-chemical, micro-emulsion, hydrothermal, aerosol, corrosive, polymer-precursory, hightemperature oxidation and others [8-16]. Existance of micro-impurities in powders, structural-morpholgical construction of particles and consolidation technologies stipulate exploitation characteristics of corundum ceramic products. During the transformation of the phases of aluminum hydrates, different forms of Al_2O_3 (α, χ, η, δ, κ, θ, γ, ρ) are obtained. By increasing temperature, specific surface decreases, because crystalline structure changes and material porosity decreases. In addition, quantity of Al-OH bonds and acidity of oxide decrease during $\gamma \rightarrow \alpha$ transformation that is often used for obtaining selective catalysts supports [17].

Aluminum content in the Earth's crust reaches 8%. As we have mentioned, it is widely used in all fields of science and technology. At present, producing of alumina in the world reaches several millions of tons and it is mainly obtained from bauxites by using the Bayer process. Many chemical compounds and ceramic materials are produced from the pure Al_2O_3. Maximum purity of Al_2O_3, obtained by Bayer process reaches 99,6-99,9%, that can be used for obtaining ceramics with different functional purposes and as substrates (Si/ Al_2O_3 , Si-Ge/Al_2O_3, As-Ge/ Al_2O_3 and others) of integral circuits. Al_2O_3 (99,99%) with higher purity is used for obtaining scintillators ($Y_3Al_5O_{12}$), single crystals (sapphire), gas sensors, electron systems components and others.

Wide-scale production of aluminum oxides of high purity is realized by the following methods:

1. Hydrolysis of aluminum alkoxides, those are based on the following chemical transformation

$$Al \xrightarrow{ROH} Al(OR)_3 \xrightarrow{H_2O} Al(OH)_3 \xrightarrow{t^oC} Al_2O_3$$

2. Chemical Vapor Deposition (CVD). By evaporation of volatile aluminum compounds ($AlCl_3$, AlR_2Cl, $AlRCl_2$, $Al(OR)_3$and others) and their oxidation (H_2O,O_2) nano-sized Al_2O_3 (50nm) is obtained, that consists of γ and α phases.

3. Decomposition of amonium-alum and of ammonium aluminum carbonate hydroxide [17-19].

$$2(NH_4)Al(SO_4)_2 * nH_2O \rightarrow Al_2O_3 + 2NH_3 + 4SO_3 + 2H_2O$$

$$2NH_4AlO(OH)HCO_3 \rightarrow Al_2O_3 + 2NH_3 + 2CO_2 + 3H_2O$$

According to experts, producing of aluminum oxide nanopowders will increase in future, because demands for it is increasing in the area of electronic industry, (semiconducting materials, energy transformers, sensors, aerospace technologies, laser technique, scintillators, abrasives, membrane filters, plasma displays, mechanical engineeringand others). As we have mentioned, one of the widespread methods for obtaining Al_2O_3 is receiving alkoxides from metallic aluminum and their hydrolysis in controlled conditions. At high temperature only α-Al_2O_3 is stable, which is obtained by gradual heating of unstable intermediate phases of aluminum hydroxides and aluminum oxides above 1200^{o}C temperature. In this case, transformation of cubic lattice into hexagonal takes place. Formation of crystals with small- size α-structure is realized at low speed, however grain growth occurs spontaneously So one of the important moments is transformation at low temperature, preliminary inclusion of α-Al_2O_3 crystals during low-temperature synthesis (in conditions of decomposition of precursor, hydrolysis, drying-heating and annealing), for obtaining ultra-dispersive α-Al_2O_3 nano-powders. It is established, that phases transition temperature of aluminum oxides is depended on the existence of seed of α-

Al_2O_3, water steam pressure and different impurities. By adding α-Al_2O_3 crystals phase transition energy decreases, existence of water steam contributes ions surface diffusion and formation of α-Al_2O_3 phase at lower temperature. Many scientific- researching centers work on this problem and lots of chemical methods are used for low temperature γ – α or θ – α phase transitions. During the low-temperature phase transformation process of agglomeration decreases, and also consolidation process of primary crystals reduces. There are several methods of solution these problems: α-Al_2O_3 was obtained at low temperatures from aluminum hydroxide compounds by adding 5% α –Al_2O_3 phase in the reactive area that plays a role of crystallization centers (seeds) [20]. Precipitation method was used for obtaining ultradispersive aluminum oxide. The following systems were studied:

I. $Al(OH)_3$ (free from nitrate ions)
II. $Al(OH)_3$+ 5% α-Al_2O_3 free from nitrate ions)
III. $Al(OH)_3$+ 45% NH_4NO_3
IV. $Al(OH)_3$+ 5% α-Al_2O_3+ 45% NH_4NO_3

It is established, from differential thermal analysis (DTA) that, by heating I and III composites (100-1300 ^oC), generation of α-Al_2O_3-phase occurs at 1220 and 1155 ^oC, respectively. By X-ray phase analysis (XRD) α-phase generates within the 1150-1200 ^oC and 1050-1150 ^oC temperature ranges. Adding of 5% α-phase in the initial components significantly decreases α-Al_2O_3-generation temperature. For II composite generation temperature reaches 1118^oC (DTA) and 600-1100^oC (XRD); for IV composite the temperatures of generation are 1009^oC (DTA) and 775-950^oC (XRD). Physical -mechanical properties of corundum ceramics, obtained from synthesized powders clearly differ from each other: particle size of the powders obtained from the first composite is ~200 nm and the temperature of consolidation of ceramics from these powders is 1600oC. For consolidation of the powders obtained from IV composites (particle size <60 nm) 1450^oC is quite enough. Ceramics density approaches 99% of the theoretic data. Thus, decrease of formation temperature of α-Al_2O_3 sharply increases consolidation conditions of corundum ceramics and physical mechanical properties of the obtained ceramics.

Particle size is changing during phase transformation [21]. It is established, that transition process of γ–Al_2O_3, obtained by polymer-precursor method, is accompanied by increase of particle sizes in α-Al_2O_3. At the initial stage from $Al(OH)_3$ is obtained $NH_4Al(SO_4)_2$, that is transferred into aluminum nitrates, then into polymer gel by adding ethylene glycol. By annealing at 500^oC a morphous powder is obtained, that forms γ–Al_2O_3 at 700^oC. It is established, that formation of α-phase begins with annealing of amorphous powder at 1000-1025^oC temperature and at 1500^oC temperature only α-phase is obtained. By XRD analysis It was established, that particles sizes of γ–Al_2O_3 at 800-950^oC were 5-10 nm, while particle sizes of α-Al_2O_3 obtained from it reached 10-100 nm (at 1050-1200^oC). With increasing of temperature, phase transition is accompanied by particle size increase [21].

α-Al_2O_3 monocrystals are obtained by annealing composition of potassium sulphate, bayerite [α-$Al(OH)_3$] and 3-8% α-Al_2O_3 nanopowders at 900^oC. Obtained α-Al_2O_3 has rounded plates shape, with 0,5-1,5μm diameter, thickness 50-150 nm. α-aluminum oxide nanopowder was included in aluminum nitrates solution, that is added solution of ammonium (pH=9) and dispesant Polyethylene glycol. To the obtained bayerite is added K2SO4 with molar ratio K /Al=3÷12. It is established, that during annealing powder phase transitions takes place:

bayerite (α-$Al(OH)_3$) ⟶ boehmite (γ -AlOOH) ⟶ γ–Al_2O_3 ⟶ α-Al_2O_3.

Specialists consider, that low-temperature synthesis of α-phase is conducted by generating liquid phases , in this case generating of $K_3Al(SO_4)_3$- takes place, that is formed in this system at 612^oC and it melts above the temperature of 654^oC. Plate's diameter decreases in the powder composition by increasing mass portion of α-Al_2O_3 nanocrysatls additives from 3% to 8% from 1000 nm to 200 nm, respectively [22].

Adding of AlF_3 causes decrease of generation temperature of α-Al_2O_3 from metastable aluminum oxides. Decrease of temperature is explained by generation of AlOF-intermediate compound, that contributes

decomposition of regular structure and formation of Al^{+3} ions vacancies by accelerating diffusion. Initial precursor was obtained by hydrothermal treatment of isopropilate, aluminum ftoride (2%) and isopropanol solutions in the autoclave at 120°C during 24 hours. It is established, that with increasing AlF_3 concentration morphology of α-Al_2O_3 powders changes from irregular to hexagonal plates formation [23].

Temperature intervals of phase transformation of aluminum oxides weakly changes with adding different rare earth metals cations in the system. It is established, that by consolidation of α-Al_2O_3 powders, containing 0,1% Lu^{+3} ions at 1400°C temperature, nanostructural corundum ceramics is formed density of which coincides with 99% of the theoretical data [24]. Transformation of cheap commercial metastable aluminum powders to the stable α-phase is possible by adding a small amount of α-Al_2O_3 nano-powders in the system and their subsequent grinding. Nanostructural ceramics obtained of these powders are characterized by high bending strength and hitting viscosity [25]. A technology for producing α-Al_2O_3 from diaspore (α-AlOOH) has been worked out [26]. Diaspore was obtained via hydrolysis of $Al(O^tBu)_3$ by HCl. Ratio of reagents alkoxide/HCl=1. In this case, at 500-800°C temperatures 64% α- and amorphous phases are obtained. Inclusion of α- diaspore crystals with concentration of $7{,}6.10^{16}$ particles/mol in the reactive area causes increase of corundum output. In this case, at 700°C temperature product of alkoxide transfers into α-Al_2O_3 phase. Generation of corundum particles begins during heating hydro-gel from 450°C. If we compare transformation of metastable forms, obtained by the Bayer process into the thermodynamically stable α-Al_2O_3 phase, we will notice, that for obtaining α-Al_2O_3 phase it is necessary to heat it up to >1100°C. Obtaining aluminum compounds and hydroxides from metallic aluminum and their subsequent low-temperature transformation into α–phase is considered as an alternative method of the Bayer's process. Disadvantage of the above mentioned method is technical difficulty and the duration of implementation process of the controllable hydrolysis during obtaining the diaspore [26].

γ–Al_2O_3 phase transformation during grinding 50 nm size powders in the planetary mill has been studied. It is established, that without inclusion of α-Al_2O_3 crystals γ-phase does not transfer into α-phase (20 h). If powder grinding is implemented by steel balls with mass ratio m(balls)/m Al_2O_3=10:1, at the room temperature, after 20-27 hours γ–Al_2O_3 transfers into α-Al_2O_3 [27].

It is established, that inclusion of α-Al_2O_3 in the reactive area promotes formation of YAG ($Y_3A_5O_{12}$) Al_2O_3 and YAG nano-threads [28]. Nano-threads were obtained by hydrolysis of aluminum and yttrium isopropilates and by adding α-Al_2O_3-particles of 200nm size in the sol-gel process. Aluminum nano-threads cause increase of ceramics thermal stability, especially due to decrease of creep.

α-Al_2O_3 nano-threads have been obtained from boehmite, when 5% α-Fe_2O_3 was included in aluminum nitrates solution, that is isostructural analogue of α-Al_2O_3. It is established, that phase transformation temperature decreases to 1025°C and particles with orientation [0001] Al_2O_3 //[0001] Fe_2O_3 and [1120] Al_2O_3// [1120] Fe_2O_3 are obtained [29].

2. EXPERIMENTAL PART

2.1 Materials

Aluminum nitrate nonahydrate (≥98%), aluminum isopropoxide (≥98%), isopropanol (99,8%), aluminim powder (99%), copper (99%), iron (99%) were purchased from Sigma-Aldrich. Other reagents are used for analytical grade.

2.2 Technics

Microstructure of the powders and the produced corundum product was studied by optical and electronic scanning microscopes (Nikon ECLIPSE LV 150, NMM-800TRF, Nanolab-7). Grain size and fraction distribution of the synthesized powder was established by Analysette 12 Dyna sizer. Phase analysis of the specimens was conducted on the X-ray difractometer DRON-3M (Cu-Kα, Ni filter, 2^O/min).

2. 3 Synthesis

Solution combustion synthesis is conducted in the following way:

To 7,5 g (0,02 mol) $Al(NO_3)_3{\cdot}9H_2O$ is added 3 g (0,05 mol) urea and 0,2 g metallic powder (Al, Cu, Fe). The mixture is stirred in the agate pestle for 10 minutes, as a result thick sticky mass is obtained, which is placed in a porcelain vessel. The vessel is placed in a muffle furnace heated up to 500˚C, where reaction mixture is self-

ignited in 2 minutes. Temperature of the mixture achieves 1500-1560˚C. Temperature is measured with IR thermometer. The reaction results in the formation of a voluminous powder.

Partial hydrolysis of aluminum isopropoxide was carried out in isopropanol with molar ratio isopropanol: aluminum isopropoxide: water =200: 1: 2 at 80˚C for 1 h. Isopropanol is moved away in rotor evaporation and Al $(NO_3)_3 \cdot 9H_2O$ is added to the obtained gel with molar ratio Al $(O^iC_3H_7)_3$: Al $(NO_3)_3 \cdot 9H_2O$= 1:1, 1. The reaction mixture is put on a porcelain vessel, which is placed in the muffle furnace heated up to 500˚C. Voluminous powder of white color is obtained. Reaction is conducted analogically, when aluminum nitrate and 5% **α-** Al_2O_3 seed powders are simultaneously introduced in the hydrolized mass.

3. RESULTS AND DISCUSSIONS

Modified polymer-precursor and solution combustion reaction were applied for obtaining α-alumina. Aluminum nitrates, aluminum alkoxides, oxidants, and bi-functional compounds producing organic-inorganic gels (glycols, aminoalcohol, carboxyl acids, aminoacids, biopolymers and others) were used as initial precursors. Organic-inorganic gels were obtained by homogenization of aluminum and organic compounds in the temperature range of 80-200°C and by carbonization of the obtained mass in the range of 300-800°C. The resulted black powder consisted of γ-alumina. Its transformation in α- alumina was conducted on the air at 1180-1200°C during 2 hours. By adding 3-5% α-Al_20_3 seeds in the initial reactive mixture γ→α phase transformation temperature (1200°C) decreases to 1020-1080°C.

One of the simple methods for obtaining α-Al_20_3 is a low temperature (400-500^{0}C) reaction between aluminum nitrate (oxidant) and organic compounds. For obtaining α-Al_20_3 there is often used interaction of aluminum nitrates and urea described by the equation:

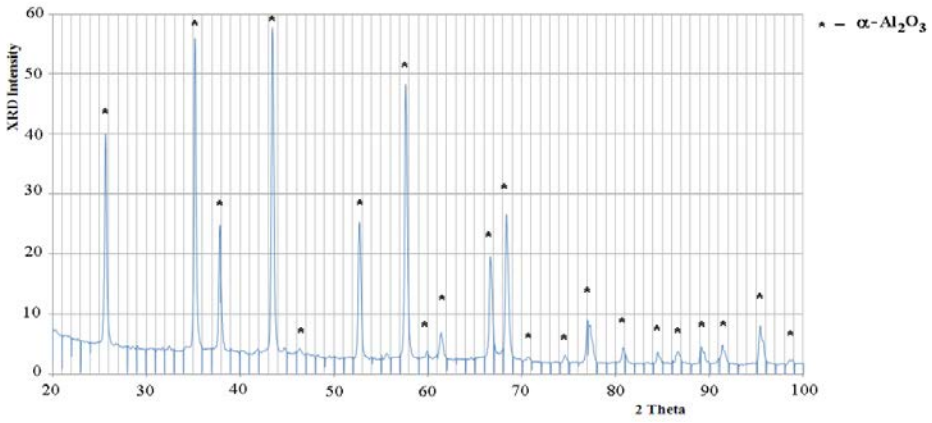


Fig.1. XRD patterns of α-Al_2O_3 obtained by interaction of aluminum nitrate and urea. Temperature of combustion reaction ~500^{0}C.

Reaction starts at 500^{0}C, it is exothermic, reactive area is heated up to ~1500^{0}C. α-Al_20_3 is obtained, which XRD pattern is given in Fig.1.

$$2\ Al(NO_3)+5NH_2CONH_2 \rightarrow \alpha\text{-}Al_20_3\ +5CO_2 +10H_2O +8N_2$$

The above mentioned equation does not describe ongoing processes, because due to a partial decomposition of aluminum nitrate on the early stage of the reaction (< 200^{0}C) (before the temperature achieves~500^{0}C, nitrogen oxides are released. The released gases contain NO_2 and O_2. Posiibillities of obtaining α-Al_20_3 from the $Al(NO_3)_3$-NH_2CONH_2–Al system have been studied. Adding of aluminum resulted in increasing the amount of aluminum oxide, because Al_20_3, obtained by annealing the mixture of $2Al(NO_3)_3 \cdot 9H_2O+5NH_2CONH_2$ made only 10% (mas) of the reactive mass. XRD analysis shows that temperature during reaction increases up to ~1500^{0}C, however aluminum powder (5-75 μm) is not oxidized and instead of α-Al_20_3 amorphous Al203 is generated (Fig.2). Heating of the remaining reaction product Al - Al_20_3 at ~750-800^{0}C for 2h promotes

generation of α-Al_20_3. This can be explained by the fact, that at 100-200^{0}C the reactive mixture forms sticky mass, which surrounds particles of aluminum powder and prevents oxygen diffusion towards aluminum surface, on the other hand during reaction large volume of gaseous substances are released causing decrease of concentration of atmosphere oxygen in the reactive area. At the same time, reaction velocity is quite high: 2-4 cm/sec. Thus, by inclusion of metallic aluminum up to 10% in the reactive mixture promotes inhibition of α-Al_20_3 generation. It is generated by heating of the reaction product for relatively a long time at ~800^{o}C temperature (Fig.3).

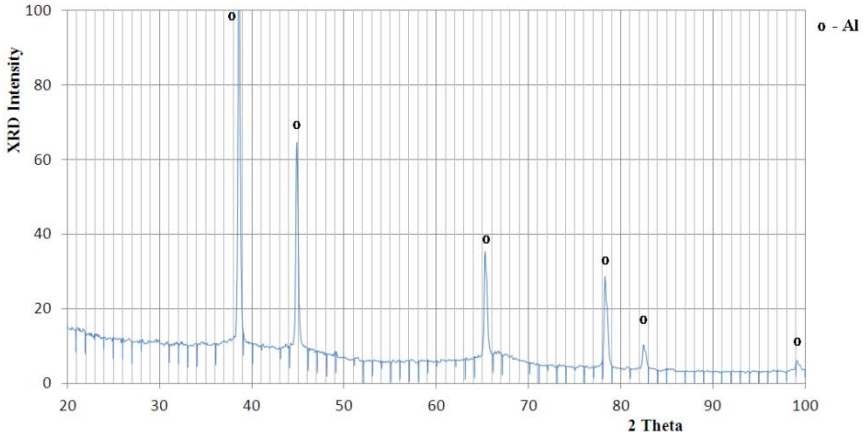


Fig.2. XRD patterns of solid residue, obtained by interaction of aluminum nitrate-urea-metallic aluminum. Temperature of combustion reaction ~500^{0}C.

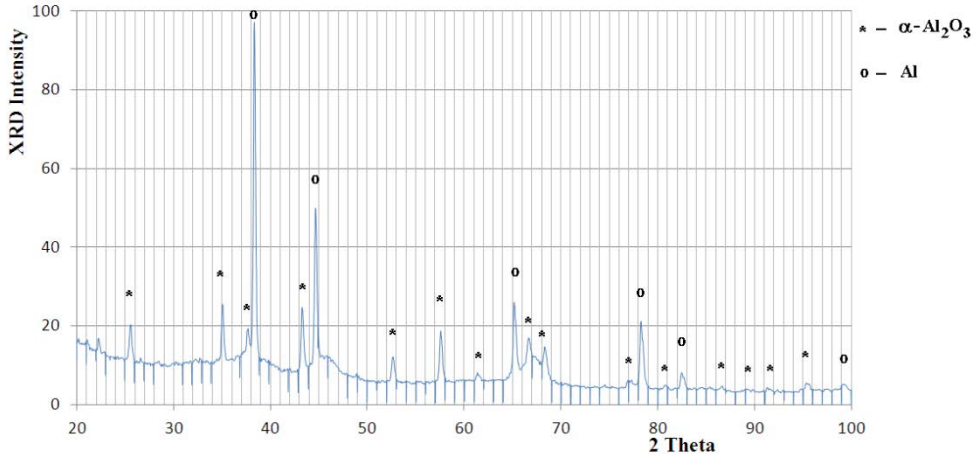


Fig.3. XRD patterns ofAl/α-Al_2O_3 composite, obtainedafter annealing at 800^{0}C (2 h) of solid residue, received by interaction of aluminum nitrate- urea-metallic aluminum.

The results of XRD data and chemical analyisis show that metallic aluminum is not oxidized in these conditions, because particles surface is covered with or thin layer of aluminum oxide, obtained as a result of the reaction. Iron and copper give different effect in the reaction mixture ($2Al(NO_3)_3 \cdot 9H_2O+5NH_2CONH_2$). Copper reacts with the reaction mixture at 150-200^{o}C and it takes green color; after ignition of the mixture black voluminous mass is formed. It does not contain metallic copper and it is mainly α-Al_20_3. By heating this mixture at ~800^{o}C for 2 h powder of reddish color is obtained with evident reflexes on the X-ray pattern; unknown phase is also revealed (Fig. 5,6). In the case of iron there are formed α-Al_20_3 at ~500^{0}C and an amorphous phase, which at~800^{o}C transfers into α-modification.

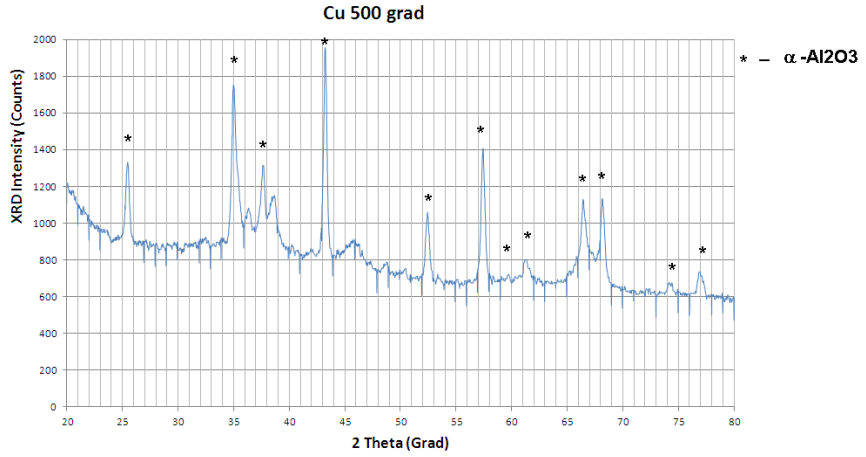


Fig.4. XRD patterns of α-Al_2O_3 obtained by interaction of aluminum nitrate-urea-copper.

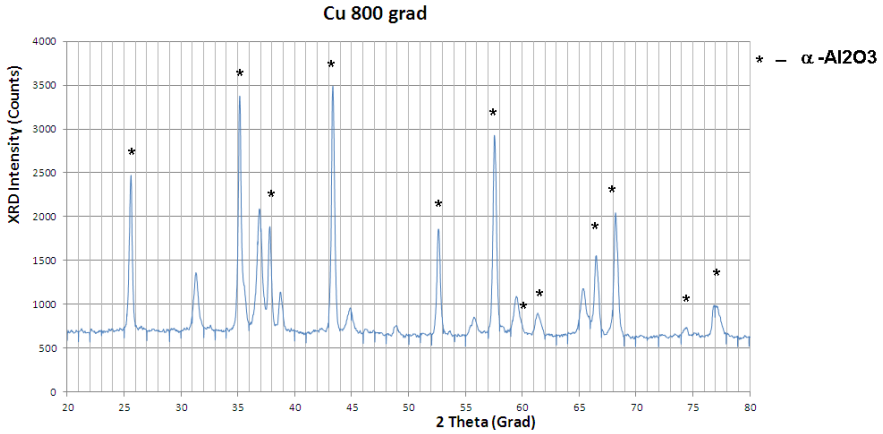


Fig.5. XRD patterns of the composite, obtained after annealing at 800^0C (2 h) of solid residues, received by interaction of aluminum nitrate- urea-copper.

Low temperature synthesis of γ- and α-Al_20_3 oxides was conducted with rapid heating of the mixture of partly hydrolyzed aluminum isopropoxide and aluminum nitrate at ~500^0C. In this case, NO_3^- ions are oxidants and reducers - isopropyl group $CH(CH_3)$], reaction is exothermic and the reaction mixture temperature reaches 800-1100^0C. XRD patterns show that the size of primary crystallits of the obtained powders is ~50 nm. Crystallite size is calculated by using Shehrer's equation:

$$\Delta(2\theta)=m\lambda/(D\cos\theta)$$

where $\Delta(2\theta)$ is full width at half maxiumum in radians;

m – factor of crystals shape;

λ – is wavelength of the radiation (nm);

Δ – grain size of crystallite (nm);

θ – Bragg's angle.

Reaction products are platelets with length- 8-15μm; density - 30-70 mg/ml. They are easily crashed with generating nanosized particles.

For preparing α-aluminum oxide powder there was used a method of corrosion of aluminum plates, activated by mercury. It is known, that surfaces of amalgamated metals are easily oxidized through generating oxides and

hydroxides respectively [15]. Possibilities of obtaining nanophase oxyhydroxide powders from aluminum at low temperatures (20-90°C) was studied. It is established, that after treatment of aluminum plates with diluted solutions of mercury (I, II) compounds (chlorides, nitrates, sulphates), fibers of $Al_2O_3 \cdot nH_2O$ are generated on thier surfaces. Their generation velocity depend on the nature of mercury compounds. The highest activity was revealed in the obtained systems based on $HgCl_2$. Generation velocity of the fiber with 7-22 μm diameter reaches 0.1-0.5 mm/min. Fibers with 5-20 mm height increase perpendicular to the plates and repeat a shape of activated aluminum surface (fig.5). Fibers increasing process was observed by optical microscope.

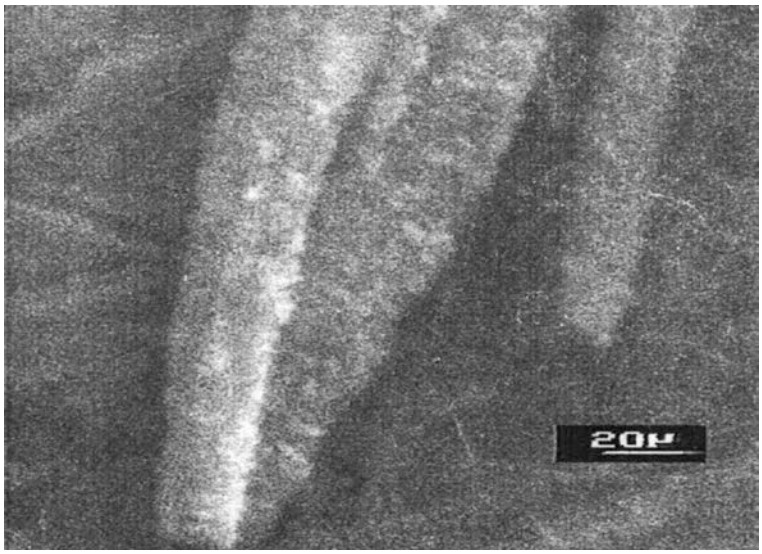


Fig.6. SEM micrograph of $Al_2O_3 \cdot nH_2O$ fibers, generated on the metallic aluminum plate.

XRD patterns (Fig.6.) show that, from the aluminum, activated at room temperature are obtained $Al_2O_3 \cdot nH_2O$ amorphous powders containing a small amount (<2% mass) of metallic aluminum (1). Genaration of crystalline phases from these powders begins at 500°C temperature (2, 3). By their subsequent heating (1000-1100°C) α-Al_2O_3 fibers consisting of 10-30 nm sizes primary crystallites are obtained (4).

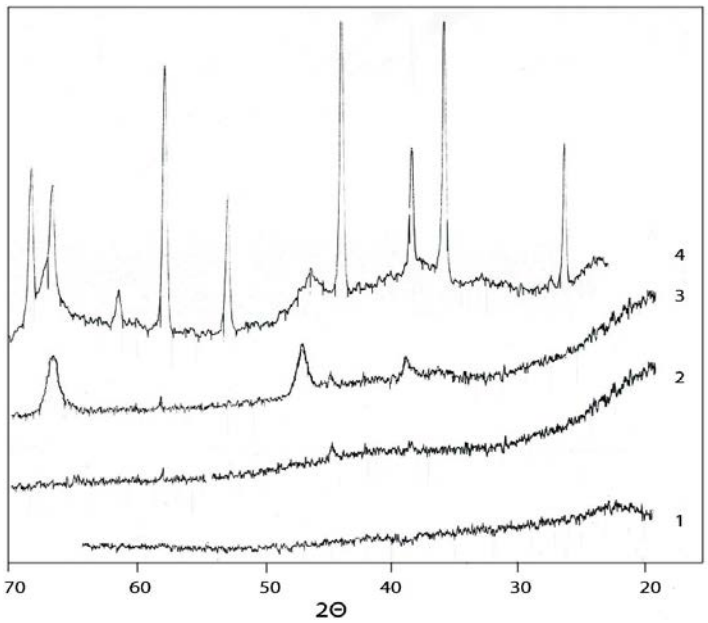


Fig.7. XRD patterns of amorphous powder $Al_2O_3 \cdot nH_2O$ after various heat treatments.

1 - 25 °C; 2- 500 °C; 3 - 800 °C; 4 - 1100°C.

4. CONCLUSIONS

Low temperature phase transformation and obtaining of α-Al_2O_3 nanopowders is possible, if in the reaction mixture is added a small amount of up to 5% α-Al_2O_3 Al_2O_3 (during decomposition, hydrolysis, drying-heating and annealing of precursors). Organic-inorganic gels were obtained by homogenization of aluminum and organic compounds within the range of 80-200°C and by carbonization of the obtained mass within the range of 300-800°C. The addition of 3-5% α–Al_2O_3 seeds in the initial reactive mixture decreases $\gamma \rightarrow \alpha$ phase transformation temperature (1200°C) to 1020-1080°C. It was established, that during the interaction between aluminum nitrates and urea, adding of aluminum caused obtaining of amorphous aluminum oxide, annealing of which for 2h at 800°C on the open air gave α-Al_2O_3. Influence of Fe and Cu on the mixture of aluminum nitrates and urea is different. They react with this mixture, but mainly α–Al_2O_3 is obtained. It was established that by low temperature corrosion (20-90^{o}C) of aluminum activated with mercury there was obtained $Al_2O_3 \cdot nH_2O$. Subsequent annealing of the amorphous powder at 1000-1100^{o}C resulted in the formation of α-Al_2O_3 fibers. XRD analysis showed that Al_2O_3 fibers contained particles with primary crystallites of 10-30 nm sizes.

REFERENCES

1. A.I. Gusev, A .A. Rempel. Nanocrystalline Materials, Cambridge Int. Sci. Publ., 2004, 351pp.

2.M. Niederberger, N. Pinna. Metal Oxide Nanoparticles in Organic Solvents. Synthesis, Formation, Assembly and Application,Springer, 2009, 215pp.

3. P. Thrower, T.W. Mason. Materials in Today's World, 3rd ed.; McGraw-Hill: New York, NY, USA, 2008.

4. T.Hanemann, D.V. Szabo. Polymer-Nanoparticle Composites: From Synthesis to Modern Applications. Materials, vol.3, 3468-3517, 2010.

5. J.F. Gerard. Fillers and Filled Polymers; Wiley-VCH: Weinheim, Germany, vol.169, 2001.

6. V.V. Ivanov, A.S. Kaygorodov, V.R. Khrustov, S.N. Paranin. Fine Grained Alumina-Based Ceramics Produced Using Magnetic Pulsed Compaction. Ceramic Materials - Progress in Modern Ceramics, 04/2012; ISBN: 978-953-51-0476-6, (In book).

7. K.A. Khalil. Advanced Sintering of Nano-Ceramic Materials, 2012, ISBN: 9789535104766, InTech, DOI: 10.5772/38287. Available from:http://www.intechopen.com

8. A. Hasmaliza, M.A. Fakhru'l-Razi, A.B. Dayang-Radiah, R. Aghababazadeh. Process for Producing Nano-Alpha-Alumina Powder, ISRN Nanotechnology, vol.2011 (2011), Article ID 692594, 5 pp.

9. V. Saraswati, G.V.N. Rao, R.G.V. Rao. Structural evolution in alumina gel, J. Mater.Sci., vol.22 (7), 2529-2535, 1987.

10. H. Hou, Y. Xie, Q. Yang, Q. Guo, C. Tan. Perapration and characterization of γ-AlOOH nanotubes and nanorods, Nanotechnol., vol.16(6), 714-721, 2005.

11. Y. Xia, Y. Yang, P. Sun, Y. Wu, B. Mayers, A. Gates, Y.Yin, F.Kim, H.Yan. Onedimensional Nan-ostructures: Synthesis, characterization, and applications, Advanced Mater., vol.15 (5), 353-357, 2003.

12. G. L. Teoh, K. Y. Liew, W. A. K. Mahmood. Synthesis and characterization of sol–gel alumina Nanofibers, J. Sol-Gel Sci. Technol., vol.44 (3), 177-180, (2007).

13. M.G. Ma, J.F. Zhu. A Facile solvothermal route to synthesis of γ-alumina with bundlelike and flower-like morphologies, Mater. Lett. vol.63, 881-885, 2009.

14. HUANGKe-long, YIN Liang-guo, LIU Su-qin, LI Chao-jian. Preparation and formation mechanismof AI_2O_3 nanoparticles by reverse microemulsion. Trans. Nonferrous Met. Soc. China, vol.17, 633-637, 2007.

15. Q. Yang, Y. Deng, W. Hu. Synthesis of alumina nanofibers by a mercury-mediated method. Ceram. Intern. vol.35 (1), 531-537, 2009.

16. B.N. Sherikar, A.M. Umarji. Compaction Behaviour of Solution Combustion Synthesized Alumina Ceramic Powders. International Journal of Emerging Technology and Advanced Engineering. vol.3 (1), 351-355, 2013.

17. T. Shirai, H. Watanabe, M. Fuji, M. Takahashi. Structural Properties and Surface Characteristicson Aluminum Oxide Powders. Materials Chemistry and Physics, vol.103, 394–399, 2007.

18. S. Fujiwara, Y. Tamura, H. Maki, N. Azuma, Y. Takeuchi. Development of New High-Purity

Alumina, "SUMITOMO KAGAKU", (transslated), v.2007-1. (2007 01 02_fth.pdf)

19. Zibo Lituo Aluminum Co., Ltd. |Calcined alumina, alumina chemicals...

www.chinaleto.com/page_en/article_disp.asp?id=83&sid= (2011).

20. S. Rajendran. Production of ultrafine alpha alumina powders and fabrication of fine grained strong ceramics. Journal of Materials Science, vol.29 (21), 5664-5672, 1994.

21. S. Cava, S.M. Tebcherani, I.A. Souza, S.A. Pianaro, C.A. Paskocimas, E. Longo, J.A. Varela. Structuralcharacterization of phase transition of Al2O3nanopowders obtained by polymeric precursor method. Materials Chemistry and Physics,vol.103, 394–399, 2007.

22. Xinghua Su, Jiangong Li. Low Temperature Synthesis of Single-crystal Alpha Alumina Platelets by Calcining Bayerite and Potassium Sulfate. J. Mater. Sci. Technol., vol.27 (11), 1011-1015, 2011.

23. Fu Gao-feng, Wang Jing, Kang Jian. Influence of AlF_3 and hydrothermal conditions on morphologies of α-Al_2O_3. Trans. Nonferrous. Met. Soc. China, vol.18, 743-748, 2008.

24. A. Odaka, T. Yamaguchi, T. Fujita, S. Taruta, K. Kitajima. Densification of rare-earth (Lu, Gd, Nd)-doped alumina nanopowders obtained by a sol−gel route under seeding. Powder Technology, vol.193 (1), 26-31, 2009.

25. Y. Yoshizawa, K. Hirao, S. Kanzaki. Fabrication of low cost fine-grained alumina powders by seeding for high performance sintered bodies. Journal of the European Ceramic Society, vol.33 (13–14), 2365-2830, 2013.

26. R.L. Smith, G.S. Rohrer, A.J. Perrotta. The Influence of Diaspore Seeding and Chloride Concentration on theTransformation of "Diasporic" Precursors to Corundum. Journal of the American Ceramic Society, 2000, October 16, Version 3/20/2000.

27. Y. Wang, C. Suryanarayana, L. An. Phase Transformation in Nanometer-Sized c-Alumina by Mechanical Milling. J. Am. Cer. Soc., vol.88 (3), 780-783, 2005.

28. A. Towata, H.J. Hwang, M. Yasuoka, M. Sando, K. Niihara. Fabrication of Polycrystalline YAG/AlUMINA Composite Fibers and YAG Fibers [pap 1277.pdf].

29. Stephen M. Sabol. Development of a Textured and Tabular Grain Microstructure in Alumina fibers via Seeded Sol-Gel Processing. (A Thesis in Ceramic Science), [sabol.pdf].