

Transformation of Aluminum Unstable Oxyhydroxides in Ultrafine α - Al_2O_3 in Presence of Various Seeds

T. Kuchukhidze, N. Jalagonia, Z. Phachulia, R. Chedia

Abstract—Ceramic obtained on the base of aluminum oxide has wide application range, because it has unique properties, for example, wear-resistance, dielectric characteristics, and exploitation ability at high temperatures and in corrosive atmosphere. Low temperature synthesis of α - Al_2O_3 is energy-economical process and it is topical for developing technologies of corundum ceramics fabrication.

In the present work possibilities of low temperature transformation of oxyhydroxides in α - Al_2O_3 , during the presence of small amount of rare-earth elements compounds (also Th, Re), have been discussed. Aluminum unstable oxyhydroxides have been obtained by hydrolysis of aluminium isopropoxide, nitrates, sulphate, and chloride in alkaline environment at 80-90°C temperatures. β - $\text{Al}(\text{OH})_3$ has been received from aluminum powder by ultrasonic development. Drying of oxyhydroxide sol has been conducted with presence of various types seeds, which amount reaches 0,1-0,2% (mas). Neodymium, holmium, thorium, lanthanum, cerium, gadolinium, dysprosium nitrates and rhenium carbonyls have been used as seeds and they have been added to the sol specimens in amount of 0.1-0.2% (mas) calculated on metals. Annealing of obtained gels is carried out at 70–1100°C for 2 hrs. The same specimen transforms in α - Al_2O_3 at 1100°C. At this temperature in case of presence of lanthanum and gadolinium transformation takes place by 70-85%. In case of presence of thorium stabilization of γ - and θ -phases takes place. It is established, that thorium causes inhibition of α -phase generation at 1100°C, and at the time when in all other doped specimens α -phase is generated at lower temperatures (1000-1050°C). Synthesis of various type compounds and simultaneous consolidation has developed in the furnace of OXY-GON. Composite materials containing oxide and non-oxide components close to theoretical data have been obtained in this furnace respectively. During the work the following devices have been used: X-ray diffractometer DRON-3M (Cu-K α , Ni filter, 2°/min), High temperature vacuum furnace OXY-GON, electronic scanning microscopes Nikon ECLIPSE LV 150, NMM-800TRF, planetary mill Pulverisette 7 premium line, SHIMADZU Dynamic Ultra Micro Hardness Tester, DUH-211S, Analysette 12 Dyna sizer.

Keywords— α -Alumina, combustion, consolidation, phase transformation, seeding.

I. INTRODUCTION

At present the greatest attention is given to using of nanotechnologies, obtaining of α - Al_2O_3 nanopowders and nanostructural ceramic materials based on them. Many methods are used for obtaining ultrafine α - Al_2O_3 , including sol-gel process, precipitation, chemical dissolution, plasma-

chemical, electrochemical, microemulsion, hydrothermal, aerosol, corrosive polymer-precursor, high temperature oxidation and others. After transformation of aluminum hydrates phases different kinds of Al_2O_3 (α , χ , η , δ , κ , θ , γ , ρ) are obtained. At high temperatures α - Al_2O_3 is formed, that is obtained by gradually heating of intermediate phases of aluminum hydroxides or alumina ~1200°C [1]-[5]. Low temperature synthesis of α - Al_2O_3 is energy saving process and is topical for improving fabrication technology of corundum ceramics. At high temperature enlargement of nanosized particle (10-70 nm) takes place up to 200-1000 nm that is undesirable process and is the main disadvantage of existing fabrication technology of α - Al_2O_3 . Therefore transformation at low temperature is one of the significant point, that implies preliminary inclusion of dopants in low temperature synthesis process (in condition of drying-heating and annealing, dissolution of precursors and hydrolyze), for obtaining ultrafine α - Al_2O_3 nanopowders [6]-[10]. At present several method of the direct obtaining of α - Al_2O_3 is known. At the lowest temperature (-550°C) diaspora transfers into thermodynamic stable form. It includes in bauxite composition and in Bayer process together with other aluminum compounds dissolves in NH_4OH and finally it is excreted in form of bayerite. Its obtaining from aluminum compounds is very difficult and expensive process [10].

The goal of the work is, obtaining of aluminum isopropoxide, nitrate and aluminum powder from the local resources; establishing of low temperature transformation possibilities of aluminum unstable oxyhydroxides into α - Al_2O_3 in the presence of rare-earth metals compounds (also other dopants) with small amount and developing technology of fabricating materials with various functional purposes from oxide and non-oxide compounds by using OXY-GON high temperature vacuum furnace.

II. EXPERIMENT

Obtaining of α - Al_2O_3 by oxidation-reduction reaction: 3g (0,05 mol) urea and dopant are added to (0,02mol) $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The mixture is stirred during 10 min, in a result thick viscous mass is received, which is poured in porcelain bowl. The bowl is placed in muffle furnace heated up to ~500°C-temperature, where it is combusted ~2 min. Temperature of mixture reaches 1500°C. Temperature is measured by IR-thermometer. In a result white bulk powder is obtained (Fig. 1).

T. V. Kuchukhidze, N. T. Jalagonia and R.V.Chedia are with Ilia Vekua Sukhumi Institute of Physics and Technology, Georgia, Tbilisi, (e-mail: tinikokuchukhidze@gmail.com, nati.jalagonia@gmail.com, sipt@sipt.org).

Z. V. Phachulia is with Sukhumi State University, Georgia, Tbilisi, (e-mail: info@sou.edu.ge).

Aluminum isopropoxide is obtained by the following chemical reaction:



Metal aluminum granules, powder and plates are washed out with ethanol, then with 5% NaOH solution, then again with $\text{C}_2\text{H}_5\text{OH}$ and are dried at 120°C . Purified aluminum is placed in ball-mills for grinding during 2 hrs. 50g alumina is taken from the obtained mass and placed in flask. Then 500ml anhydrous isopropanol, with 2 g hydrazine (II) chloride is poured in the flask. Reaction mixture is boiled and 0.2 g iodine crystals are added. From the reaction mixture excess alcohol is removed and 260g $\text{Al}(\text{OCH}(\text{CH}_3)_2)_3$ is obtained. Secondary distillation of the obtained isopropoxide is conducted from 0.5l flask. 245 g aluminum isopropoxide is obtained, which is crystallized after cooling. It is established from X-ray –fluorescence analysis, that quantity of other metals impurity is lower than $10^{-2}\%$.

Obtaining of $\alpha\text{-Al}_2\text{O}_3$ powder: Sol of unstable aluminum oxohydroxide was obtained by hydrolysis of $\text{Al}(\text{OC}_3\text{H}_7)_3$. 30g aluminum isopropoxide is dissolved in 540ml water and is heated at $80\text{--}85^\circ\text{C}$ in condition of constant stirring approximately 6-8 hrs. Then for peptization 1-2ml HNO_3 and dopants are added and continue stirring for 3hrs at 110°C . Water is removed from the obtained sol and xerogel is dried at $\sim 120^\circ\text{C}$. Obtaining of ultrafine $\alpha\text{-Al}_2\text{O}_3$ from xerogel was conducted by its annealing from the room temperature up to 1250°C in high temperature furnace by the following temperature regime: from 25°C up to 500°C with velocity of $3^\circ\text{C}/\text{min}$, from 500°C up to 1000°C with velocity of $5^\circ\text{C}/\text{min}$, and up to 1250°C temperature with velocity of $10^\circ\text{C}/\text{min}$. Annealing of aluminum and obtaining of $\alpha\text{-Al}_2\text{O}_3$ was conducted with the analogous regimes.

Obtaining of corundum product by hot pressing method in OXY-GON furnace: powdery composites are preliminary heated on the air up to 1200°C (2 hrs). Powders are placed in preliminarily annealed (1400°C) graphite molds, which are covered inside with graflex plate. The plate is covered with thin layer of boron nitride. Graphite mold is placed in high temperatures vacuum furnace (OXY-GON) and powder is pressed under 500 kgf loading. The chamber is cooled by water, which temperature does not exceed 20°C . After vacuuming the chamber it is heated according to the preliminarily established regimes up to 1500°C and after this powders are pressed under maximal loadings 10 000 kgf. This pressure is maintained for 60–70 min. Maximum temperature of sintering is 1600°C (1 hrs). Cooling of graphite molds is conducted in vacuum by $5^\circ\text{C}/\text{min}$ velocity. After cooling below 100°C temperature pure argon is included in the chamber. Obtained corundum product is black, because thermal dissociation of Al_2O_3 and formation of defect crystalline lattice take place in vacuum. In purpose of whitening of the sample it is annealed on the air at $1500\text{--}1600^\circ\text{C}$ during 2 hrs.

III. RESULTS AND DISCUSSIONS

Easy method of obtaining $\alpha\text{-Al}_2\text{O}_3$ is often used in laboratory practice that is based on the interaction between aluminum nitrates and organic compounds (Solution Combustion Synthesis) [11], [12]. In this case NO_3^- ions are oxidizers, and organic compounds, including amines and their products, oxyacids, alcohols, carbohydrates, urea and its products, oligomers and polymers are reducers. The cheapest compound is urea. Initiation temperature of reaction is $450\text{--}500^\circ\text{C}$. The reaction is exothermic and temperature of reaction mixture reaches $800\text{--}1500^\circ\text{C}$. Temperature of reaction mixture changes according to oxidizers/reducers ratio. Reaction speed is rather high 2-4cm/sec. Bulk density of obtained α -alumina powder reaches 30-70 mg/ml (Fig. 1). They are easily fragmented and nanosized particles are generated [13].



Fig. 1 Obtaining $\alpha\text{-Al}_2\text{O}_3$ powder from $(\text{NO}_3)_3\text{-NH}_2\text{CONH}_2$ compound by oxidation-reduction reaction

Disadvantage of this method is small content of alumina in large amount of reaction mixture ($\sim 10\%$ mas). We have studied possibilities of obtaining $\alpha\text{-Al}_2\text{O}_3$ from $\text{Al}(\text{NO}_3)_3\text{-NH}_2\text{CONH}_2\text{-Al}$ system. Inclusion of aluminum aimed at increasing alumina, because after $2\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + 5\text{NH}_2\text{CONH}_2$ reaction oxidizers are allocated: nitrogen (IV) oxide and oxygen. Despite, the reaction temperature reaches a $\sim 1500^\circ\text{C}$, aluminum powder (5-75 mkm) does not oxidizes. $\alpha\text{-Al}_2\text{O}_3$ is obtained by annealing reaction product ($\text{Al}+\text{Al}_2\text{O}_3$ amorphous) at 800°C (2hrs). It is established, by X-ray –phase and chemical analysis, that metal aluminum does not oxidizes in such conditions, because particles surface is covered by alumina layer, formed in a result of reaction.

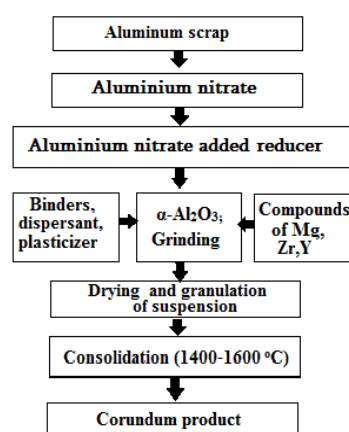


Fig. 2 Simplified scheme of obtaining corundum products from aluminum scrap

Based on α - Al_2O_3 powders obtained by oxidation-reduction reaction, pressing powdery composites α - Al_2O_3 - MgO , α - Al_2O_3 - Y_2O_3 - MgO , α - Al_2O_3 - Y_2O_3 - ZrO_2 and others were synthesized. Dopants MgO , Y_2O_3 , ZrO_2 were included in reaction mixture in different forms of nitrates. Optimal temperature regimes of pressing have been chosen for each composite.

It is established by structural-morphological studies that sizes of primary crystals of powders are within 50-300nm and they generate large sized easily breakable agglomerates (1-3 μm).

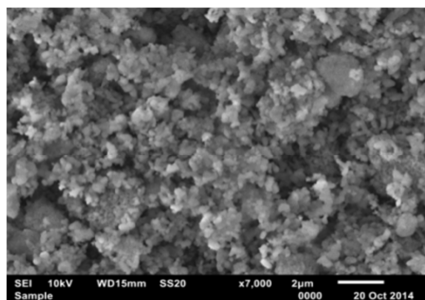


Fig. 3 Micro images of α - Al_2O_3 - Y_2O_3 - ZrO_2 powdery composites

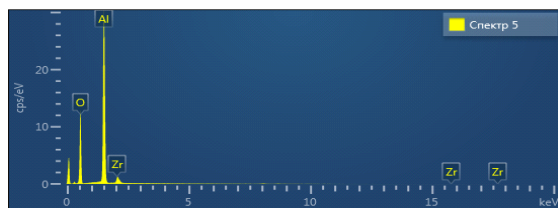


Fig. 4 Energy-dispersive micro-X-ray spectrum of α - Al_2O_3 - Y_2O_3 - ZrO_2 powdery composite

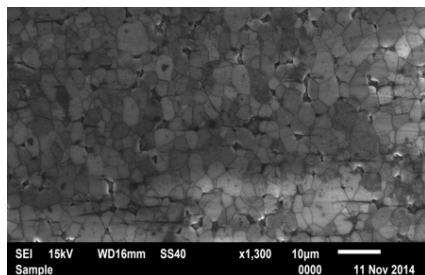


Fig. 5 Micrographs of ceramic composites obtained at 1600°C (Al_2O_3 - ZrO_2 - MgO)



Fig. 6 Corundum ceramics materials with different compositions and experimental specimens fabricated from them

Aluminum isopropoxide was synthesized from metal aluminum scrap, and after its hydrolysis unstable aluminum oxohydroxides and oxides are obtained. Ultrafine α - Al_2O_3 is obtained by sol-gel method according to the following scheme (Fig. 7).

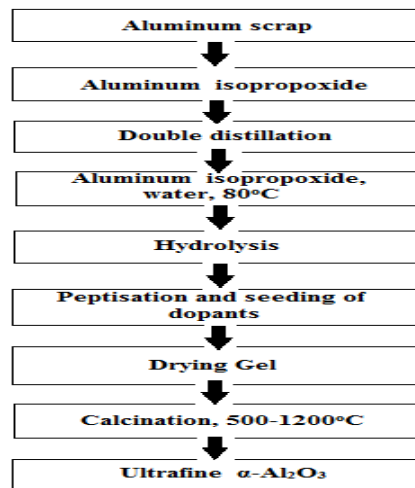


Fig. 7 General scheme of obtaining ultrafine α - Al_2O_3 by sol-gel method

In a result of hydrolyze aluminum isopropoxide, mixture of aluminum oxohydroxides ($\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) are generated and its peptization is conducted by adding nitric acid. Nitrates of cerium, holmium, thorium, gadolinium, dysprosium, lanthanum and neodymium are added to sol (0.1-0.2% mas.) calculated on metal. Drying of dopant-added gel is conducted at 120°C. It is established; that gel does not contain non-hydrolyzed Al-O-C bonds. Thermal treatment of obtained xerogel was conducted at 120°C (a), 500°C (b) and at 800 °C (c) for 2 hrs (Fig. 8).

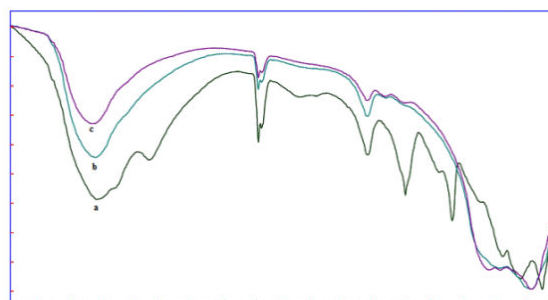


Fig. 8 IR spectra of gels obtained aluminum isopropoxide annealed at different temperatures (a-120°C, b-500°C, c-800°C)

It is shown from IF spectra, that in all three samples in area of 3429-1635 cm^{-1} absorption sols of O-H are revealed, and in area of 476-758 cm^{-1} -Al-O coordination bonds are observed.

It is established from DSC, that xerogel dried at 120°C, absorbs water vapor on the air, and then desorbs it by heating at 60-150°C. At 300-500°C temperatures intensive condensation of hydroxide group and desorption of water take place (Fig. 9). All samples are characterized with dehydration

of aluminum oxohydroxides and generation of unstable alumina. They mainly consist of γ and θ phases.

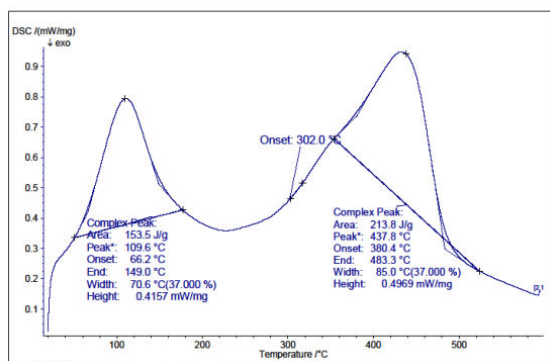


Fig. 9 Differential scanning calorimetry curve (DSC, 20-600°C) of aluminum oxohydroxide obtained by sol-gel method

Influence of lanthanum, cerium, neodymium, gadolinium, dysprosium, holmium and thorium ions on the transformation of unstable aluminum compounds into in alpha-alumina were studied. It is established from X-ray-phase analysis, that in a presence of holmium, formation of α - Al_2O_3 begins at temperature lower than 1000°C and at 1100°C temperature it transfers in α - Al_2O_3 (Fig. 10).

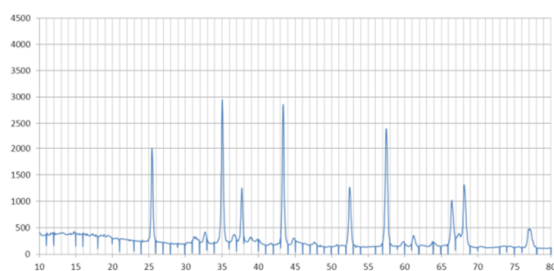


Fig. 10 Transformation of metastable aluminum oxo-hydroxide in alpha-phase by adding holmium nitrate (1100°C)

In a presence of lanthanum, dysprosium, cerium and gadolinium transformation at 1100°C takes place by 70-85%. And in a presence of thorium, stabilization of gamma and theta-alumina phases takes place (Fig. 11), while in samples doped with all other metals the same phase generates at lower temperatures (1000-1050°C).

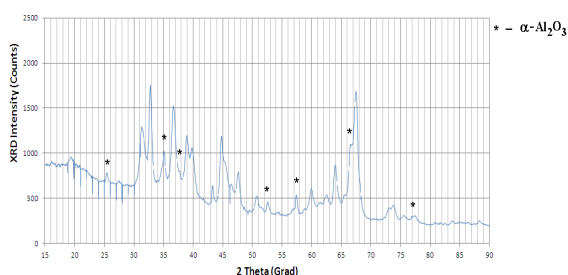


Fig. 11 Transformation of metastable aluminum oxohydroxide in alpha-phase by adding thorium nitrate (1100°C)

Selective obtaining of metastable aluminum compounds is difficult task. One method of obtaining aluminum hydrate-bayerite is ultrasonic development of aluminum powder at 70-90°C in ammonium hydroxide solution. We studied influence of adding neodymium nitrate on generation and transformation processes of unstable oxo-hydroxides. It is established, that by adding neodymium compound in alkaline environment bayerite is obtained from metal aluminum and by adding rhenium carbonyl-boehmite is received (Fig. 12). After their thermal treatment (70-1100°C) transformation of unstable phases into alpha-alumina takes place: neodymium and rhenium containing powders completely transfer into α - Al_2O_3 , while from powder without dopant, mixture of α and γ phases is obtained (Fig. 13). Thus, adding of promotes formation of alpha-alumina.

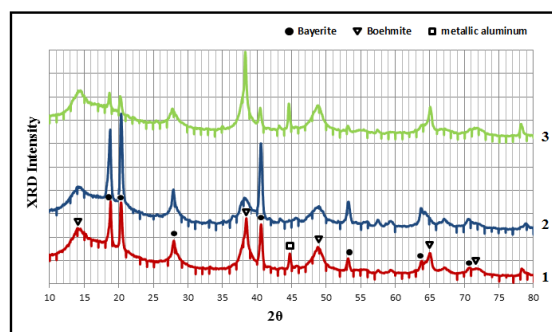


Fig. 12 X-ray of unstable oxohydroxides obtained from metal aluminum in ammonium hydroxide solution at 85°C: 1. Without dopant, 2. dopant-neodymium nitrate, 3. dopant-rhenium carbonyl

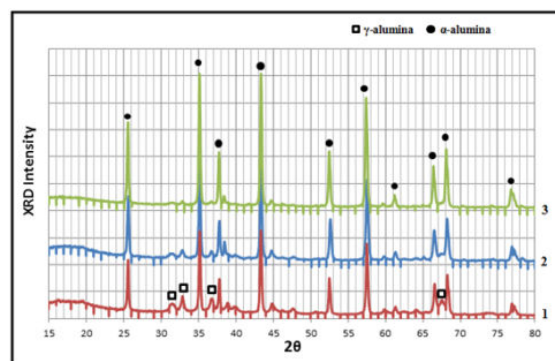


Fig. 13 X-ray of unstable oxohydroxides obtained from metal aluminum in ammonium hydroxide solution at 85°C: (powders are annealed at 1100°C): 1. Without dopant, 2. dopant-neodymium nitrate, 3. dopant-rhenium carbonyl

IV. CONCLUSIONS

In the present work obtaining of aluminum isopropoxide, nitrate and aluminum powder from scrap aluminum and their further transformation in α - Al_2O_3 have been studied. It is shown possibilities of low temperature transformation of aluminum oxyhydroxides in α - Al_2O_3 during the presence of small amount of rare-earth elements compounds (also other dopants). Low temperature synthesis of α - Al_2O_3 is energy

saving process and it is quit actual for perfection of technology of corundum ceramics production.

Technology for obtaining corundum ceramics was developed which is based on simultaneous pressing and consolidation methods of powdery composites in high temperature vacuum furnace OXY-GON. Besides, implementation of solid-phase reactions is possible in the furnace. Corundum ceramic products were obtained by sintering at 1600°C (1 hr), which is characterized by high strength, microhardness and fracture resistance, absence of open porosity, corrosion resistance. Their density achieves 99,5-99,6% of the theoretical.

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