SYNTHESIS AND CHARACTERIZATION OF ALUMINA NANO-POWDER OBTAINED BY SOL-GEL METHOD

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Este cunoscut că metoda sol gel este una din metodele neconvenționale de obținere a pulberilor ceramice. În studiul realizat s-a avut în vedere obținerea şi caracterizarea de nanopulberi de Al_2O_3 prin metoda sol-gel, aceasta putand fi un potential material utilizat la realizarea de implanturi biocompatibile.[1,2,3,4] In vederea sintezei s-a pornit de la precursori de natură chimică diferită – anorganici (clorură de aluminiu, $AlCl_3$) şi organici (triizopropilat de aluminiu, $(C_3H_7O)_3Al$. Pulberile obținute în urma uscării gelului au fost tratate termic la 1000°C şi 1200°C, palier 2 ore. În vederea caracterizării din punct de vedere al gradului de cristalinitate şi al dimensiunii de cristalit s-a utilizat difracția de raze X (XRD). Caracterizarea microstructurală şi morfologică s-a realizat cu ajutorul tehnicilor electrono-microscopice – microscopie electronică de baleiaj (SEM) şi de transmisie (TEM).

It is known that sol-gel method is an alternative method to produce ceramic powders. The present study deals with the synthesis and characterization of Al_2O_3 nanopowders which can be a potentially utilized material for biocompatible implants.[1,2,3,4] Based on sol-gel method, the synthesis started from different chemical nature precursors – inorganic (aluminum chloride, $AlCl_3$) and organic (aluminum triisopropylate, $(C_3H_7O)_3Al$). The powders obtained after drying the gel were heat treated at 1000°C and 1200°C for 2 hours. X-ray diffraction was used in order to characterize the powders in terms of their crystallinity degree and crystallite size. Microstructural and morphological characterization was performed using electron-microscopic techniques - scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Keywords: alumina, sol-gel method, nanoparticle

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1. Introduction

Alumina is one of the inert biomaterials used in implants. It is therefore, a biodegradable material, well tolerated by the biological environment. In literature, there is information on obtaining Al_2O_3 by sol-gel method using the different precursors: aluminum triisopropylate in a hydrolysis system consisting of octanol and acetonitrile [5], aluminum nitrate – in aqueous medium [6,7], aluminum secondary butoxide - in an alcoholic medium [8].

The sol-gel method is based on the phase transformation of a sol obtained from metallic alkoxides or organometallic precursors. This sol which is a solution containing particles in suspension is polymerized at low temperature, in order to form a wet gel. The solvent is removed by drying the gel and the next step is a proper heat treatment.

Some of the advantages of the sol-gel method are its versatility and the possibility to obtain high purity materials, the provision of an easy way for the introduction of trace elements, allowance of the synthesis of special materials and energy savings by using low processing temperature.

The aim of the present paper is to prepare alumina by sol–gel method, starting from different chemical nature precursors. It is expected that the obtained alumina powders have nanometric dimensions and can be utilised as biomaterials.

2. Experimental procedure

The two precursors used in the synthesis of Al_2O_3 by sol-gel method were of different chemical nature: inorganic – aluminium chloride ($AlCl_3$) and organic – aluminium triisopropylate $(C_3H_7O)_3Al$.

2.1. In the case of $AlCl_3$ (p.a., Fluka) as precursor, the sol-gel synthesis consisted in the preparation of a 0.1 M $AlCl_3$ ethanolic solution (p.a., Chemical Company). By adding a 28% NH_3 solution (p.a. Fluka) a gel was formed. The gel was let to maturate for 30 hours at room temperature and then dried at 100^{o}C for 24 hours.

2.2. For $C_9H_{21}AlO_3$ (p.a., Fluka) used as precursor, the sol-gel synthesis consisted in the preparation of a 0.1 M $(C_3H_7O)_3Al$ ethanolic solution (p.a., Chemical Company). A 28% NH_3 solution (p.a., Fluka) was added in order to form a gel. Mild shaking at 90^{o}C for10 hours was utilised. The gel was let to maturate at room temperature for 24 hours, and then dried at 100^{o}C for 24 hours.

The resulting gels were calcined in a furnace for 2 hours (heating rate 20^{o}C/min.), at temperature values of 1000^{o}C and 1200^{o}C.

2.3. Characterizations of the powders

For identifying the crystalline mineralogic phases of the powders obtained from gels, both by drying and heat treating, and bring information on their

crystallinity degree, X-ray diffraction analysis was carried out on a Shimadzu diffractometer XRD 6000 - Ni-filtered CuKα (λ = 1.5406 Å) radiation, scanning speed of 0.02º/min, in 2θ = 10-70 deg. range.

Thermogravimetric analysis (DTA and TG) was performed using a TGA/ SDTA 851e Mettler Toledo instrument. The dry powder was heated up to 1000°C, with a temperature growing rate of 10°C/minute, using pure alumina as reference.

The micrographs were obtained using a Hytachi scanning microscope and Tecnai TM G2 F30 S-TWIN transmission electron microscope (from FEI-The Netherlands), equipped with STEM/HAADF detector, EDS (Energy Dispersive X-ray Analysis) and EFTEM-EELS (Electron Energy Loss Spectroscopy), with the folowing characteristics: acceleration voltage of 300 kV obtained from a Shottky Field emitter, TEM point resolution of 2 Å, TEM line resolution of 1.02 Å.

3. Results and discussion

3.1. X-ray Diffraction

Figs. 1 and 2 show X-ray diffraction images for the powders obtained from different precursors, dried and heat treated for 2 hours at temperature values of 1000°C or 1200°C. It should be noticed that when $AlCl_3$ was used as a precursor, the dried gel highlights the presence of $AlCl_3 \cdot 6H_2O$ crystal (ICDD 73-0301), (Fig. 1a). Thermal treatment at 1000°C for two hours leads to its decomposition with the formation of a mixture of γ-Al_2O_3 (ICDD 29-0063) and α-Al_2O_3 (ICDD 48-0366), (Fig. 1b) [5]. Increasing the temperature of heat treatment up to 1200°C for two hours results in the formation of only α-Al_2O_3 (ICDD 48-0366), (Fig. 1c) [5].

In the case of the organic precursor $(C_3H_7O)_3Al$, a poorly crystalline dried gel can be observed (Fig. 2a), revealed by a halo in the small angles interval. Thermal treatment at 1000°C leads to the formation of an $\alpha + \gamma$ - Al_2O_3 mixture (ICDD 48-0366, ICDD 29-0063),, having relatively low degrees of crystallinity (the halo at 30-45 degrees). Increasing the heat treatment temperature to 1200°C leads to the formation of α-Al_2O_3 (ICDD 48-0366) and a higher crystallinity [5]. The crystallite size values of α-Al_2O_3 are shown in Table 1. It should be observed that, as the heat treatment temperature increases, the crystallite size increases, this increase being more important in the case of the organic precursor. Irrespective of the precursor used, thermal treatment at 1200°C leads to crystallite sizes of approximately the same value.

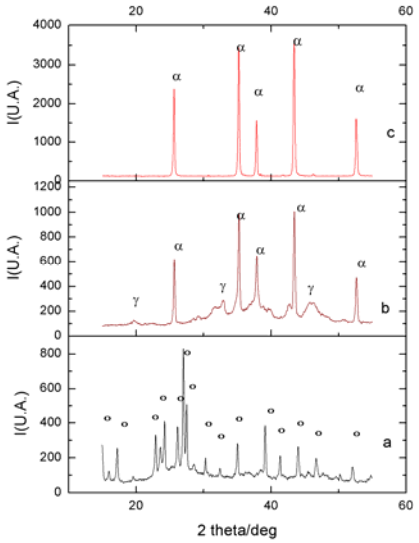


Fig. 1. The XRD pattern of alumina powder obtained by sol-gel method from aluminum chloride ($AlCl_3$), dried 100°C/24h (a), heat treated at 1000°C/2h (b), heat treated at 1200°C/2h (c): ○ – $AlCl_3 \cdot 6H_2O$ (ICDD 73-0301), α – α Al_2O_3 (ICDD 48-0366), γ – γ Al_2O_3 (ICDD 29-0063)

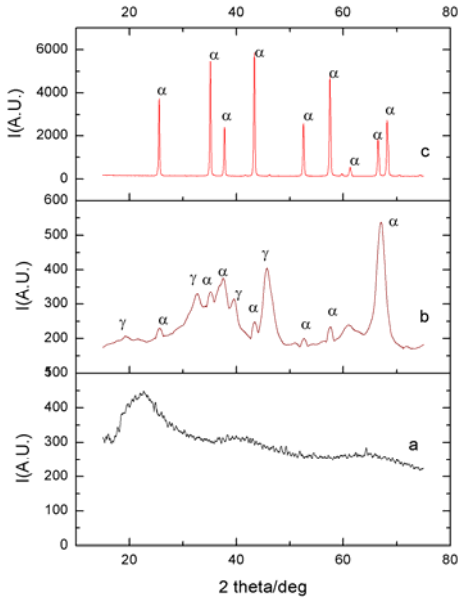


Fig. 2. The XRD pattern of alumina powder obtained by sol-gel method from aluminum triisopropylate $(C_3H_7O)_3)Al$, dried 100°C/24h (a), heat treated at 1000°C/2h (b), heat treated at 1200°C/2h (c): α – α Al_2O_3 (ICDD 48-0366), γ – γ Al_2O_3 (ICDD 29-0063)

Debye-Scherrer relation was used to calculate cristallite average dimensions of alumina powders obtained by sol-gel process using inorganic and organic precursors (Table 1).

Table 1

Dimensions of α-Al_2O_3 crystallites calculated with Debye-Scherrer relation

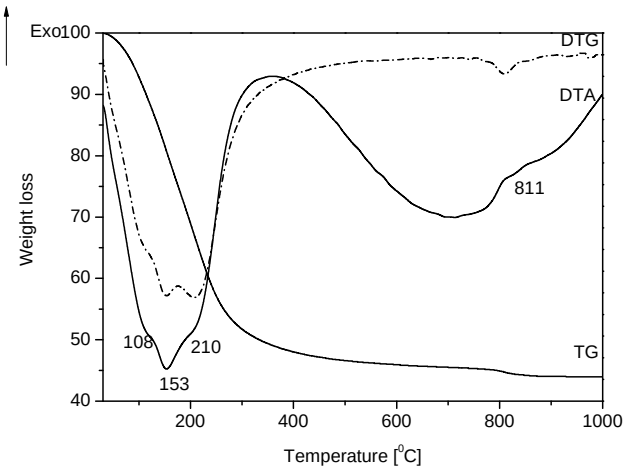
Precursor	Heat treatment temperature, (^oC)	The size of crystallites (nm), corresponding to interplanar distance d_1=3.46 Å	The size of crystallites (nm), corresponding to interplanar distance d_2=2.54 Å	The size of crystallites (nm), corresponding to interplanar distance d_3=2.08 Å	Average crystallite size (nm)
$AlCl_3$	1000	10.85	10.57	10.68	10.70
	1200	12.35	12.28	12.15	12.26
$C_9H_{21}AlO_3$	1000	2.81	2.30	2.98	2.70
	1200	12.31	12.35	12.39	12.35

3.2. Thermal analysis

Thermal analysis of the dried powders (100^{o}C/24 hours) is illustrated in Fig. 3.

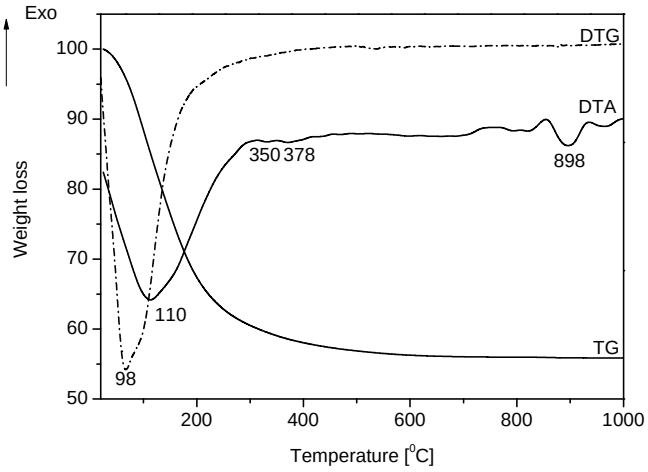
In Fig. 3a, the DTA curve recorded five endothermic effects accompanied by weight loss, the total weight loss being 55.57%. The first three endothermic effects of greater magnitude can be attributed to moisture water loss (the effect at 108^{o}C) and to hydroxyl loss from the decomposition of hydrated aluminum chloride and aluminum hydroxide, which can be possibly formed (the effects at 153^{o}C and 210^{o}C, respectively).

In Fig. 3b, the DTA curve recorded four endothermic effects, including those in the temperature range 100^{o}C - 400^{o}C, accompanied by weight loss; total weight loss is 44.03%. The endothermic effect at 100^{o}C (110°C) can be attributed to moisture water loss, while those at 350^{o}C and 375^{o}C can be attributed to the organic component decomposition. The endothermic effects at about 811^{o}C and 896^{o}C (Fig. 3a) may be attributed to the transformation of polymorphous enantiotrope γ-Al_2O_3 in α-Al_2O_3. γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ transformation temperature, with values less than 1000^{o}C, can be explained by the small degree of crystallinity and crystallite size characteristic to the nanopowders.



a

Fig. 3. (a) Complex thermal analysis of alumina powder obtained by sol-gel method from $AlCl_3$, dried 100°C/24h



b

Fig. 3. (b) Complex thermal analysis of alumina powder obtained by sol-gel method from $(C_3H_7O)_3)Al$, dried 100°C/24h

3.3. Scanning electron microscopy

Information on morphological and textural characteristics of the powders obtained by sol-gel method was made by scanning electron microscopy analysis.

Scanning electron microscopy images of alumina powders obtained by sol-gel method starting from inorganic and organic precursors, heat treated at 1000^{o}C for two hours, are given in Figs. 4 and 5.

SEM images of alumina obtained by sol-gel method starting from aluminum chloride as precursor, heat treated at 1000^{o}C for two hours, evidentiate a fine particulate matter; without being able to assess the size of the particles, it can be apreciated that they form aggregates different geometries with rounded edges (Fig. 4). SEM images of the alumina powder obtained from aluminum triisopropylate as precursor show a similar morphology to that of alumina obtained from aluminum chloride, with the observation that the particles are more homogenous and their dimensions are more reduced (Fig. 5). That is why, in order to assess a detailed analysis of their morphology, transmission electron microscopy analysis was further used.

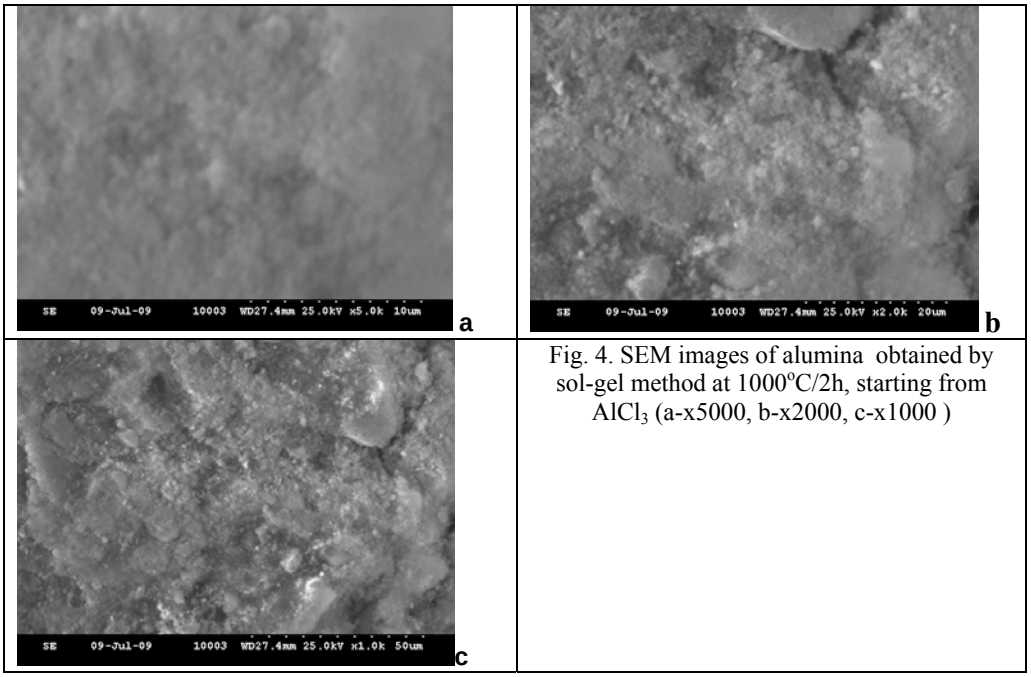


Fig. 4. SEM images of alumina obtained by sol-gel method at 1000^{o}C/2h, starting from $AlCl_3$ (a-x5000, b-x2000, c-x1000)

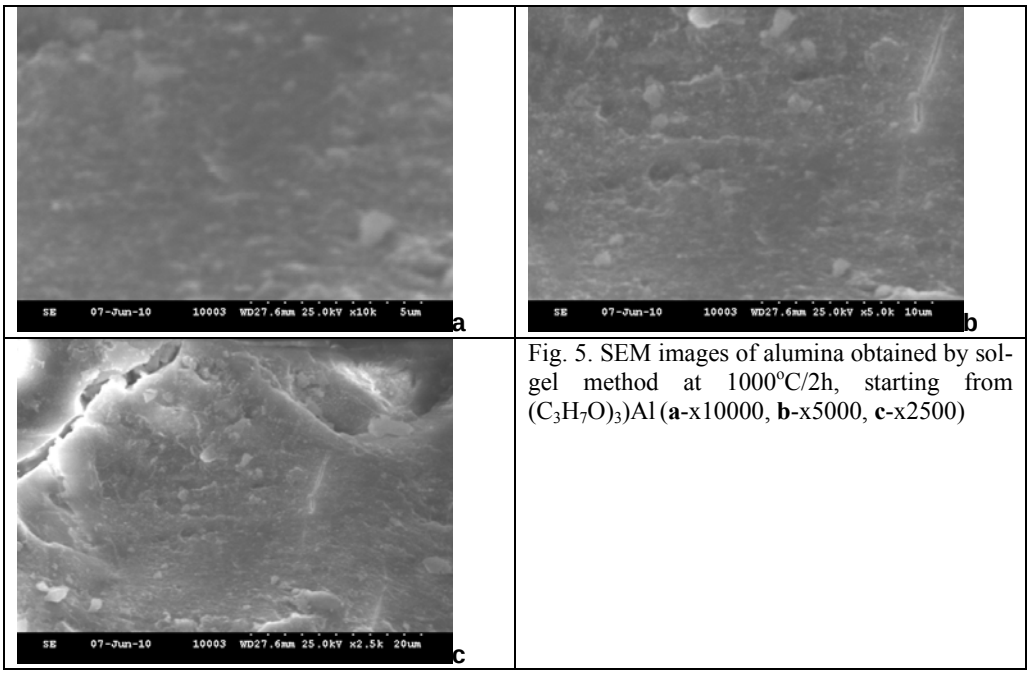
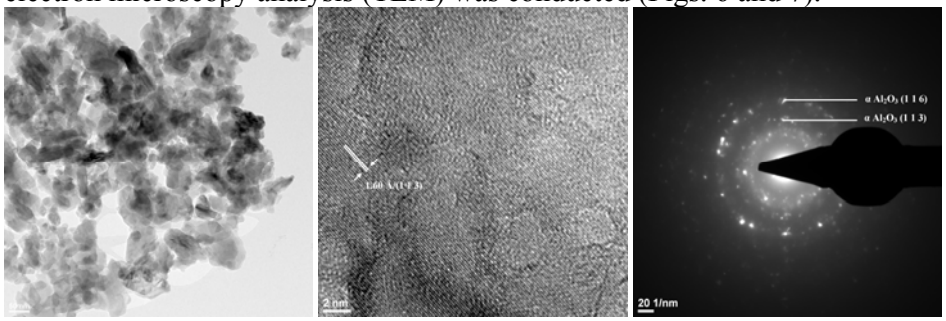


Fig. 5. SEM images of alumina obtained by sol-gel method at 1000°C/2h, starting from $(C_3H_7O)_3)Al$ (**a**-x10000, **b**-x5000, **c**-x2500)

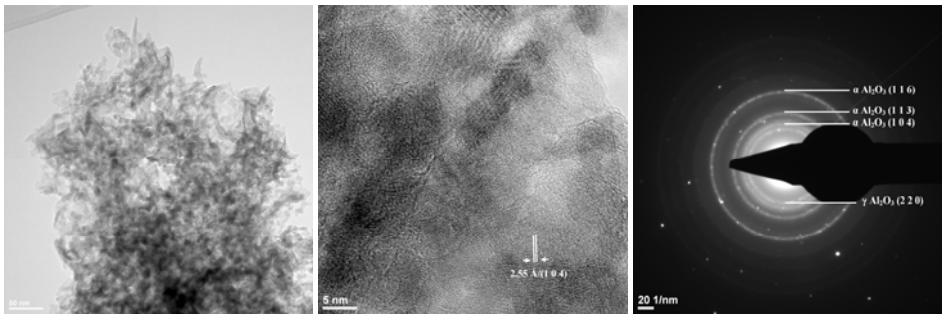
3.4. Transmission electron microscopy

In order to better put in evidence the particle size of alumina powders obtained by the sol-gel method, heat treated at 1000°C for two hours, transmission electron microscopy analysis (TEM) was conducted (Figs. 6 and 7).



a **b** **c**

Fig. 6. a - Bright field TEM image of alumina obtained at 1000°C/2h, started from $AlCl_3$, b - High resolution TEM image of alumina obtained at 1000°C/2h, c – SAED (Selected area electron diffraction) image of alumina obtained at 1000°C/2h



a **b** **c**

Fig. 7. a - Bright field TEM image of alumina obtained at 1000°C/2h, started from $(C_3H_7O)_3)Al$, b - High resolution TEM image of alumina obtained at 1000°C/2h, c - SAED (Selected area electron diffraction) image of alumina obtained at 1000°C/2h

Fig. 6a presents the transmission electron microscopy (TEM) micrographs of alumina powder obtained from aluminum chloride solution (0.1M), heat treated at 1000°C for two hours. There are two types of particles with different geometries, namely: needle shaped particles with average particle size below 25 nm and spherical particles with average size below 20 nm. HRTEM image (Fig. 6b) highlights, besides α-Al_2O_3 crystallized particles (d = 1.60 Å, corresponding plan (116)) and γ-Al_2O_3, a large amount of amorphous material. The image obtained by selected-area electron diffraction analysis (Fig. 6C) evidentiates two crystallographic planes for α-Al_2O_3: the first one corresponding to the distance between planes of 1.60 Å (116) and the second one, to the distance between planes of 2.08 Å (113).

TEM microscopy images for alumina powder obtained from aluminium triisopropylate, heat treated at 1000°C for two hours (Fig. 7a) show that the powder consists of particle clusters having acicular shape, with average particle size below 15 nm. The SAED image (Fig. 7c) highlights that the powder shows a high degree of crystallinity, with planes clearly emphasizing the crystallization of α-Al_2O_3 (104), (113), (116) and of γ-Al_2O_3 (220). HRTEM image (Fig. 7b) shows that the distance between two atomic layers is d = 2.55 Å, corresponding to the (104) crystallographic plane of α-Al_2O_3. These TEM microscopy data correlate with X-ray diffraction data results.

4. Conclusions

The sol-gel method synthesis of α-alumina starting from aluminum chloride and aluminum triisopropylate as precursors was carried out relatively easily. The resulting alumina powders were characterized by X-ray diffraction, differential thermal analysis and thermogravimetry (DTA, TG), scanning electron

microscopy (SEM) and transmission electron microscopy (TEM). Applying a heat treatment at temperatures higher than 1000oC leads to obtaining crystalline α alumina as single phase. Using sol-gel method and heat treatment at 1000oC for two hours alumina powder was obtained at the nanometric scale, both for the inorganic and organic precursor utilised. Alumina powders obtained at the nanometric scale, may have superior properties as compared to the powders obtained in larger particle sizes and can be used in medical applications as a biomaterial.

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