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Tailoring alumina thin film properties using hydrophilic/hydrophobic copolymer additives

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Thin films of alumina were deposited onto aluminium-treated substrates by pneumatic spray pyrolysis at 250 °C. As precursors, solutions of $AlCl_3$ dissolved in the mixture water : ethanol = 1 : 1 were used. As morphology controlling agents, maleic acid based copolymers (HFB/HFL) and/or acetylacetone were added in spraying solutions. The absorptance (α) and emittance (ε) values are those expected for alumina films, as possible matrix in a cermet, used as a solar-thermal selective absorber. The films have amorphous–crystalline structure and porous morphology. The alumina film composition and crystallinity can be tailored by adding acetylacetone in the spraying solution, when predominantly amorphous structures are obtained. The addition of hydrophobic/hydrophilic copolymer in the precursor solution favours the obtaining of porous aggregates with large, open structures (3.5–4 μm). These porous morphologies are suitable for further infiltration of metallic particles, for preparation of alumina-based cermets.

1 Introduction Nowadays, alumina (Al_2O_3) thin films are considered materials of interest because of their excellent properties, such as high dielectric constant, high thermal conductivity, low permeability of alkali ions, high hardness (Mohs 9) and high chemical and thermal stability. Due to these properties, alumina thin films have a wide range of applications: microelectronic devices, refractory, anticorrosive and antireflection coatings [1, 2], catalysis sensors [3], waveguide lasers [4], buffer layers for superconductors [5] and ceramic–metal composites (cermets) [6, 7]. More recently, the possible applications of alumina-based composites (bioceramic materials) in bioengineering, for the production of temporary or permanent implant devices, were reported [8]. Thin films of alumina have been prepared by various physical and chemical vapour deposition techniques, such as magnetron sputtering [9], filtered vacuum arc [10], electron beam evaporation [11], metal organic chemical vapour deposition (MOCVD) [1] and plasma-enhanced chemical vapour deposition (PECVD) [12]. Amorphous or a mixture of amorphous and crystalline alumina thin films can be easily prepared by chemical spray pyrolysis deposition (SPD) [11, 13]. SPD can be considered one of the simplest, lowest-cost and up-scalable techniques used for the deposition of nano-, mezzo- or microstructured layers with controlled properties. Within this approach, SPD is a suitable method for the preparation of alumina-based cermets with properties strongly dependent on alumina layer properties, especially thickness and morphology. These properties can be tailored by varying the precursor composition (aluminium ion concentration, solvents and additives) and the deposition parameters (temperature, number of spraying sequences, etc.). In this work, we report the preparation and characterization of alumina thin films deposited by pneumatic spray pyrolysis onto aluminium substrates, at 250 °C, from solutions of $AlCl_3$ (0.15 M) in water : ethanol (1:1) mixture. The influence of the precursor solution composition, obtained by addition of different additives (acetylacetone and copolymers with maleic anhydride), on the composition, surface morphology and optical properties (α and ε) of the alumina films required for further preparation of alumina-based cermets (Al_2O_3/NiO_x/Ni), used as solar-thermal selective absorbers, was studied.

2 Experimental

2.1 Reagents and substrates Solutions containing $AlCl_3 \cdot 6H_2O$ (95–99.8%, Scharlau Chemie) dissolved in a mixture of water : ethanol = 1 : 1, in volumes, were used as precursors. Deionized water (W) and absolute ethanol (Et, 99.9%, Scharlau Chemie) were used as solvents. In the spraying solutions were added, as morphology controlling agents (Ad), volumes (2.5 ml) of acetylacetone (AcAc, 99%, Sigma Aldrich), hydrophobic copolymer (sodium maleate–methyl methacrylate, HFB) and hydrophilic copolymer (sodium maleate–vinyl acetate, HFL), prepared at "Petru Poni" Institute, Iasi, Romania. The synthesis of the two copolymers was reported elsewhere [14].

The precursor solutions with 0.15 M concentration were sprayed onto preheated aluminium substrates (30 mm × 15 mm × 0.5 mm, 99.5%, Beofon Bucuresti). Aluminium was used as substrate for the alumina thin film deposition, because of its good thermal conductivity, low cost and good properties in a cermet-based solar absorber. The metallic substrates (A) were ultrasonically cleaned with ethanol and then immersed in HNO_3 10% solution for 24 h (A0) in order to increase the substrate surface roughness, thus favouring the alumina film growth.

2.2 Deposition method and parameters The alumina thin films were deposited onto aluminium substrates by pneumatic spray pyrolysis, which has been previously described [15]. The deposition was performed in open atmosphere at 250 °C (deposition temperature). The nozzle–substrate distance ($H = 20$ cm), the pressure of carrier gas (air, $p = 1.4$ bar) and the number of spraying sequences (55) were kept constant during all deposition processes. The breaks between two spraying pulses were varied from 30 s to 60 s. All the deposition parameters were previously optimized [16].

2.3 Characterization methods The alumina thin films were investigated by X-ray diffraction (XRD, Bruker AXS D8 with Cu K_α radiation), Fourier transform infrared (FTIR) spectrophotometry (Spectrum BX Perkin Elmer spectrophotometer, $\lambda = 2500-16000$ nm), UV–VIS spectroscopy (Lambda 25 Perkin Elmer spectrophotometer, $\lambda = 190-1100$ nm) and atomic force microscopy (AFM/STM NTEGRA Probe Nanolaboratory microscope).

3 Results and discussion The thickness and optical properties (solar absorptance, α, thermal transmittance, ε) of alumina films deposited by pneumatic spray pyrolysis, at 250 °C, from precursor solutions containing different organic additives, are shown in Table 1. The average value of the film thickness (d) was calculated from the interference effects in UV-VIS transmittance spectra using the relation [11]

$$d = \frac{\lambda_2 \lambda_1}{2n(\lambda_2 - \lambda_1)}, \qquad (1)$$

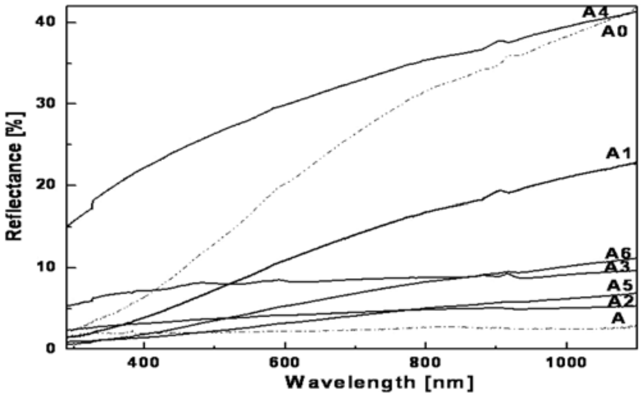

Figure 1 Reflectance UV–VIS spectra of alumina thin films (samples A1–A6) deposited onto Al substrate (A) treated with HNO_3 10% (A0).

where n is the refractive index of the alumina thin film ($n = 1.66$ at $\lambda = 300$ nm [17]) and λ_1 and λ_2 are the wavelength positions of two successive interference minima. The solar absorptance (α) of alumina films was calculated [18] from reflectance spectra recorded in the wavelength range 290–1100 nm, Fig. 1, using a UV–VIS spectrophotometer. The thermal emittance (ε) of as-deposited films was determined by measuring the spectral reflectance in the spectral range from 2500 nm to 16500 nm with a FTIR spectrophotometer, model Spectrum BX. The reflectance values in the wavelength 1100–2500 nm were estimated by interpolation.

As observed from Table 1, the alumina thin film absorptance value increases from 0.607 (sample A4) to 0.889 (sample A5), almost following the average thickness: from 276.6 nm (sample A4) to 525.4 nm (sample A2). The films' emittance values are conveniently low (excepting film A3), as is expected for a refractory material. The further embedding of metal particles will improve both optical properties.

In order to evaluate the alumina thin film composition, X-ray diffraction patterns were recorded for samples A1–A6 (Fig. 2). At the deposition conditions, no significant differences can be observed, all the films containing a mixture of amorphous and crystalline phases.

Table 1 Influence of the precursor solution composition on thickness (d) and optical properties (α, ε) of alumina thin films prepared by pneumatic spray pyrolysis.

sample	precursor solution $AlCl_3/W:Et:Ad_{(V)}$	d^* [nm]	α	ε
A1	1 : 1 : 0	354.3	0.787	0.011
A2	10 : 10 : 1(AcAc)	525.4	0.881	0.035
A3	10 : 10 : 1(HFB)	292.2	0.841	0.153
A4	10 : 10 : 1(HFL)	276.6	0.607	0.041
A5	10 : 10 : 1(AcAc) : 1(HFB)	488.2	0.889	0.058
A6	10 : 10 : 1(AcAc) : 1(HFL)	510.1	0.857	0.057

* d represents the average thickness of alumina thin films (samples).

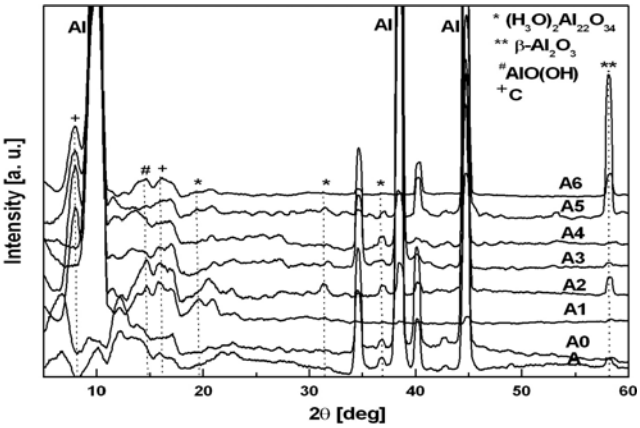

Figure 2 XRD patterns of alumina thin films (samples A1–A6) deposited onto Al substrate (A) treated with HNO_3 10% (A0).

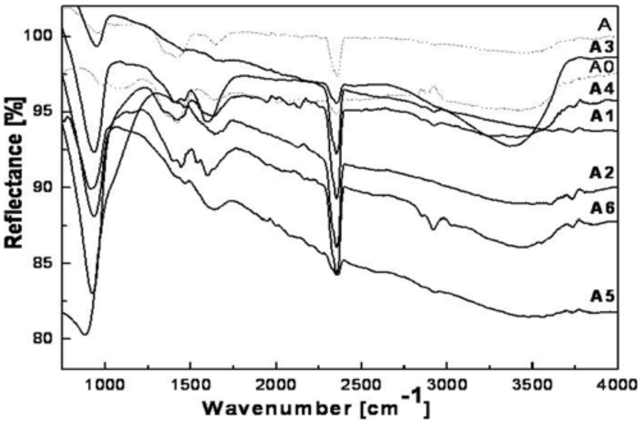

Figure 3 Reflection FTIR spectra of alumina thin films (samples A1–A6) deposited onto Al substrate (A) treated with HNO_3 10% (A0).

The predominant amorphous phase is alumina, confirmed by Refs. [12, 13] and FTIR spectra (Fig. 3).

The polycrystalline phases identified in the diffractograms can be attributed to hexagonal $(H_3O)_2Al_{22}O_{34}$ (PDF 01-070-1204), orthorhombic AlO(OH) (PDF 01-074-1895) and β-Al_2O_3 with hexagonal structure (PDF 00-010-0414). In addition, all the samples contain an amount of carbon (graphite, PDF 01-074-2328) from the high carbon content of the additives and/or solvent used in spraying solutions. The films A1, A2, A5 and A6 have higher carbon content, due to the presence of an extra sharp peak at $2\theta = 7.9°$ (absent in the X-ray spectra of aluminium and treated aluminium substrates). The carbon content, varying from 11.4% (sample A5) to 49.2% (sample A1), results from thermal decomposition of the organic additives (AcAc and HFB/HFL) and/or, in a lower extent, of ethanol in spraying solution. Considering the further applications, the graphite content does not represent a drawback since C has also a very good heat storage capacity. It also may be responsible for the good emittance values, $\varepsilon = 0.011–0.058$.

In addition, FTIR spectroscopy confirms and extends the information obtained from X-ray diffraction analysis, related to the alumina films composition. Figure 3 shows the reflection FTIR spectra of alumina thin films A1–A6 deposited onto a treated Al substrate (A0). Generally, all these spectra show two main absorption bands: 920–950 cm^{-1} (attributed to amorphous Al_2O_3 [10]) and 1500–1750 cm^{-1} (due to carboxylate groups [12]). The broad absorption band around 3000 cm^{-1} (samples A1 and A6) can be caused by Al–OH bonds associated through hydrogen bonding [12]. The stretching vibrations of terminal Al=O and Al–O that appear in FTIR spectra of films A3 ($\bar{\nu} = 881$ cm^{-1}) and A6 ($\bar{\nu} = 650–881$ cm^{-1}) can be attributed to the film surface, which is passive at lower substrate temperatures (<400 °C) [11].

Depending on the spraying solution composition, porous surface morphology alumina films (Figs. 4 and 5), with different pore size and distribution, are obtained by SPD, at 250 °C.

The surface morphology of sample A2 is different and has the largest estimated open structure varying from the other three samples, due to its predominantly amorphous (glassy) structure. The root mean square (RMS) surface roughness is 112.5 nm. The pore aggregates develop large, open structures of 1.2–3.7 µm able to host metal particles in the final cermet. The films A1, A5 and A6 surface morphology shows a certain distribution of the pore aggregates, from 3.5 µm (A6) to 4 µm (A5), for a RMS surface roughness of 153.4 nm (A6) and 200.6 nm (A5). It is obvious that the addition of organic additives, such as AcAc and

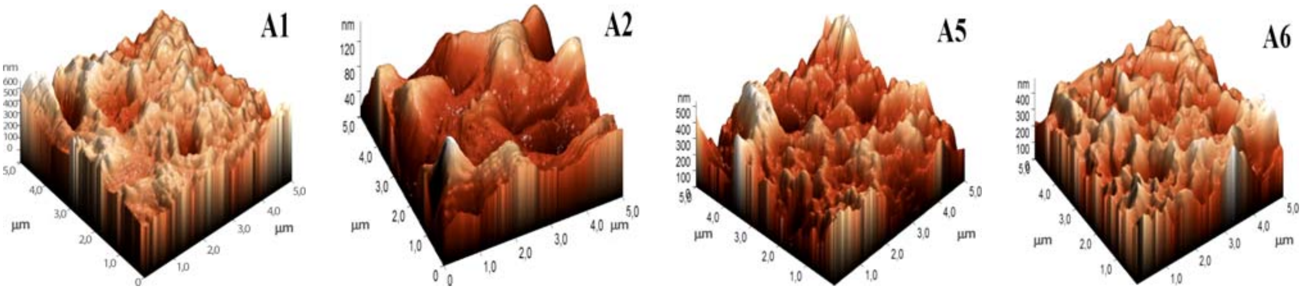

Figure 4 (online colour at: www.pss-a.com) AFM images of alumina thin films deposited onto treated Al substrates from solutions containing $AlCl_3$ in W : Et = 1 : 1 (A1), $AlCl_3$ in W : Et : AcAc = 10 : 10 : 1 (A2), $AlCl_3$ in W : Et : AcAc : HFB = 10 : 10 : 1 : 1 (A5) and lCl_3 in W : Et : AcAc : HFL = 10 : 10 : 1 : 1 (A6).

HFB/HFL copolymers, in aqua : ethanolic precursor solutions strongly influences the surface morphology of alumina thin films. The hydrophilic polymer favours the development of more regular structures, due to a stronger interaction with the Al^{3+} ions in solution (complexation) and, consequently, a lower growth rate. This assumption is confirmed by the different surface aspect of the layers obtained using only AcAc and HFB when, due to a lower nucleation and a higher growth rate, the surface is more fractured and the structure has larger openings. This can be considered an important tool in tailoring alumina thin film morphology, in order to obtain porous films, which can be infiltrated with metal and metal oxide particles for the preparation of a cermet structure, as a component in a solar absorber needed for a solar-thermal panel.

4 Conclusion

Porous alumina thin films were deposited onto Al-treated substrates at 250 °C, via pneumatic spray pyrolysis, from precursor solutions containing hydrophilic or hydrophobic copolymers and/or acetylacetone. The absorptance values are in the range 0.607–0.889 and increase almost in the same way with the film thickness. The low emittance values are expected for alumina and may be also due to the carbon content of the films. According to X-ray patterns and FTIR spectra, the films are a mixture of amorphous–crystalline phases, with Al_2O_3 as predominant amorphous phase. Depending on the additives used in the precursor solutions, porous alumina thin films with different pore sizes are obtained. The HFL copolymer favours the development of regular open structures, while fractured large open structures are developed when HFB copolymer is added in the precursor solution.

The addition of AcAc in the spraying solution can be a tool in tailoring composition and crystallinity of alumina thin films by favouring the obtaining of films with predominantly amorphous structure. The addition of AcAc and HFB/HFL copolymers in the precursor solution can be a tool in tailoring both crystallinity and morphology of alumina thin films prepared by pneumatic spray pyrolysis.

Further works on these films are currently in progress, with the aim to elucidate the film formation (nucleation and growth) from precursor solution containing HFL/HFB copolymers and/or AcAc as additives.

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