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SYNTHESIS OF ALUMINA THIN FILMS BY SPRAY PYROLYSIS

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The paper reports the obtaining and characterization of alumina thin films deposited by spray pyrolysis technique (SPD) from aqua-ethanol solutions of $AlCl_3$. The optical properties (solar absorptance and thermal emittance), film thickness and surface morphology were studied as function of the deposition parameters: substrate temperature and spraying sequence number. The results prove that the solar absorbtance is depending on both parameters while high values of the thermal emittance (ε>0.1) are recorded for all samples. The study shows that, in the deposition conditions, amorphous alumina is formed and the film roughness decreases with the temperature increase. At higher temperature due to by-products elimination, the films homogeneity is improved.

INTRODUCTION

The efficiency in solar–thermal energy conversion systems strongly depends on the materials used as absorber coatings, especially on their optical properties and thermal stability. The performance absorbers used for hot water production use a spectrally selective surface that absorbs and converts solar radiation into heat. An efficient solar selective surface is defined as having a high absorptance (in ideal case, α_{sol}=1) in the spectrum range λ = 0.3 – 2.5 μm and a low emittance (in ideal case, ε_T=0) in the spectrum range λ = 2.5 – 20 μm. Spectral selective surfaces are classified into six types: intrinsic, semiconductor-metal tandems, multilayer absorbers, ceramic-metal composite coatings, textured surfaces, and selectiv solar-transmitting coating on a blackbody-like absorber.[1] High performing selective surfaces already exists on the market but they are expensive due to the chemicals and methods used for their synthesis. The costs can be reduced by using cheap and low quantities of materials and also low-cost synthesis methods.

The aim of our work is to obtain a high performance, chemically stable and low cost spectrally selective coating of cermet type by using a low-cost technique – spray pyrolysis deposition. Cermets, ceramic–metal composite, consist of a metal oxide coating (*e.g.* Al_2O_3) containing metal nano-particles (*e.g.* Ni) embedded.[2] Due to the combination of materials, the cermets have large heat storage capacity (due to the ceramic matrix) and low thermal emittance (due to the metal). The ceramic matrix must have a controlled morphology, able to be further infiltrated with metal nano-particles and good thermal properties.

The aluminium oxide is used as ceramic matrix because of its high chemical and thermal stability. Alumina thin films can be prepared by various techniques including physical vapour deposition,[3] sputtering,[4] plasma enhanced chemical vapour deposition,[5] metal-organic chemical vapour deposition,[6] and spray pyrolysis deposition (SPD).[7] The SPD is a low-cost and versatile method used for the metal oxide layers deposition on large areas with different geometries. Within this approach, SPD is suitable for the preparation of efficient, time-resistant and inexpensive alumina thin films, with application in alumina-based cermets. Moreover, by varying the precursors' solution concentration and deposition parameters (temperature, number of spraying sequences, spraying distance etc.) alumina film properties can be tailored according to the further applications.

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In the present work, alumina films were obtained by SPD onto glass substrates, at temperatures varying from 220 to 320ºC. Aqueous-ethanolic solutions of $AlCl_3$ were used as precursors. In order to obtain alumina films with porous morphology, required for further infiltration of metallic particles, acetylacetone was added in spraying solutions. The influence of the deposition parameters (temperature, annealing and spraying sequences number) on the optical and structural properties of the obtained films has been investigated.

EXPERIMENTAL

Aqua:ethanol (H_2O: Et = 1:1, in volume ratio) solutions of $AlCl_3 \cdot 6H_2O$ (98%, Scharlau Chemie) were used as precursors for the alumina films preparation. As morphology controlling agent, 2.5 mL of acetylacetone (AcAc, 99.9%, Sigma Aldrich) were added in the spraying solutions. The precursor solutions with 0.15 mol/L concentrations were sprayed onto preheated glass substrates (1.5 cm x 3 cm x 0.15 cm, Menzel-Liaser), previously cleaned in ethanol, in an ultrasonic bath.

The deposition was done in open atmosphere at different temperatures (T = 220 - 320^{o}C), using various number of spraying sequences (n_{sp} = 30-55) with breaks of 30 seconds. The nozzle-substrate distance (H=20cm) and the carrier gas pressure (air, p=1.4 bars) were kept constant during all deposition processes. After spraying, the sample deposited at 220^{o}C, using 30 spraying sequences, was annealed in air at 400 ^{o}C for 3 h.

The films structure and composition were investigated using an X-ray diffractometer (Bruker-AXS- D8) with CuKα radiation, in the range 2θ =10–80^o. The surface morphology of the samples was studied with atomic force microscopy (AFM/STM, NTEGRA Probe Nanolaboratory) using a "GOLDEN" silicon cantilever (NCSG10, force constant 0.15 N/m, tip radius 10 nm) - contact mode.

The normal reflectance of obtained samples was measured in the wavelength interval 0.3–17 µm. A Perkin-Elmer Lambda 25 spectrophotometer was used in the wavelength interval 0.3–1.1 µm. The infrared wavelength interval, 2.5–17 µm, was covered with a Perkin-Elmer FT-IR spectrophotometer, model Spectrum BX. The measurements were combined to create one spectrum. The reflectance values in the wavelength 1.1 – 2.5 µm were estimated by interpolation.

The solar absorptance (α_{sol}), theoretically defined as a weighted fraction between absorbed radiation and incoming solar radiation in the wavelength interval 0.3– 2.5 µm, was calculated using equation 1[8]. The solar spectrum, I_{sol}, is defined according to the ISO standard 9845-1 (1992) with an air mass of 1.5.

$$\alpha_{sol} = \frac{\int_{0.3}^{2.5} I_{sol}(\lambda)(1-R(\lambda))d\lambda}{\int_{0.3}^{2.5} I_{sol}(\lambda)d\lambda} \quad (1)$$

The thermal emittance (ε_T), defined as a weighted fraction between emitted radiation and the Planck black body distribution (Ip) in the wavelength interval 2.5–20 µm, was calculated using equation 2.[8] The interval 17–20 µm is extrapolated from reflectance.

$$\varepsilon_T = \frac{\int_{2.5}^{20} I_p(\lambda)(1-R(\lambda))d\lambda}{\int_{2.5}^{20} I_p(\lambda)d\lambda} \quad (2)$$

The average value of the films thickness (d) was calculated from the UV-VIS reflectance spectra using the well-known relation:[9]

$$d = \frac{N\lambda_1\lambda_2}{2(\lambda_2-\lambda_1)\cdot(n^2-\sin^2\alpha)^{1/2}} \text{ [nm]} \quad (3)$$

where n is the refractive index of alumina thin film (n = 1.66 at λ=300nm[10]), N is the number of the fringes observed from wavelength λ_1 to λ_2 ($\lambda_1 < \lambda_2$), λ1 and λ2 are the wavelength positions of two successive interference minima and α is the angle of incidence (6º).

RESULTS AND DISCUSSION

The influence of the substrate temperature and precursor solution composition on the film thickness and optical properties (α, E_g) of alumina films obtained via SPD, from aqueous and aqueous-ethanolic (H_2O: $Et_{(V)}$ = 1:1) solutions of $AlCl_3$ with different concentrations (c = 0.1-0.2 mol/L) has been previously studied.[11,12] It was observed that higher solar absorbance (α = 0.4-0.6) and large band gap energy (E_g = 5.09-7.31 eV) values were obtained for alumina films deposited from solutions containing $AlCl_3$ (c = 0.15 mol/L) in water:ethanol = 1:1 mixture.

The influence of the deposition parameters (substrate temperature - T_{sub}, spraying sequence number - n_{sp}) on average film thickness (d), optical properties (α, ε) and roughness of alumina films obtained by SPD, from precursor solution with optimized concentration and composition, is presented in Table 1.

a) The influence of deposition parameters on the film thickness and optical properties

To investigate **the influence of spraying sequence number (n_{sp})** on film properties, a lower n_{sp} =30 (G1) and a higher n_{sp}=55 (G3) spraying sequence number were tested. The film thickness slowly decreases as the spraying sequence number increases; this behaviour can be explain by the fact that, a higher number of spraying sequences represents a higher stationary time on the heater that increases the probability of by-products elimination (H_2O or HCl from AlO(OH) or AlOCl) formed at lower temperature.

Table 1

The thickness and optical properties (α, ε) of alumina films obtained by SPD

Sample	T (°C)	n_{sp}	d (nm)	α	ε	Roughness (nm)
G1	220	30	624	0.85	0.20	192
G2*	220	30	427	0.91	0.18	219
G3	220	55	572	0.86	0.14	135
G4	270	55	547	0.87	0.16	89
G5	320	55	501	0.89	0.15	26

* G1 sample annealed at 400°C for 3 hours

The films deposited below 200 °C were found to be non-uniform, therefore, to study **the influence of the substrate temperature** on the film properties the temperature was varied from 220 to 320°C. The films deposited at higher temperature are thinner compared to films deposited at lower temperature; this can be correlated with reordering in film structure that occurs at higher temperature. The removal of interlayer water from decomposition of AlO(OH) leads to the formation of Al_2O_3 denser layers.

The substrate temperature and the spraying sequence number have a major influence on the optical properties (solar absorbance and thermal emittance) of the alumina films. The solar absorbance values of the Al_2O_3 layer are improved by increasing the substrate temperature (T = 320 °C) and by annealing. This can be correlated with re-arrangements in the films deposited at higher temperature, when the film homogeneity is improved. For all samples, the thermal emittance values are higher than accepted (ε>0.1), but further infiltration with metal particles is expected to strongly decreases the ε values.

b) The influence of deposition parameters on the film composition

The X-ray diffraction analysis confirms and extends the information obtained from reflectance spectra. The XRD patterns of alumina films deposited at different temperatures (T = 220-270 °C), using different number of spraying sequences (30, 55), are presented in Figure 1. As references, XRD patterns of glass substrate and a crystalline powder, containing Al_2O_3 (ICDD, PDF 01-078-2427) and AlOOH (ICDD, PDF 01-074-1895) phases, were used.

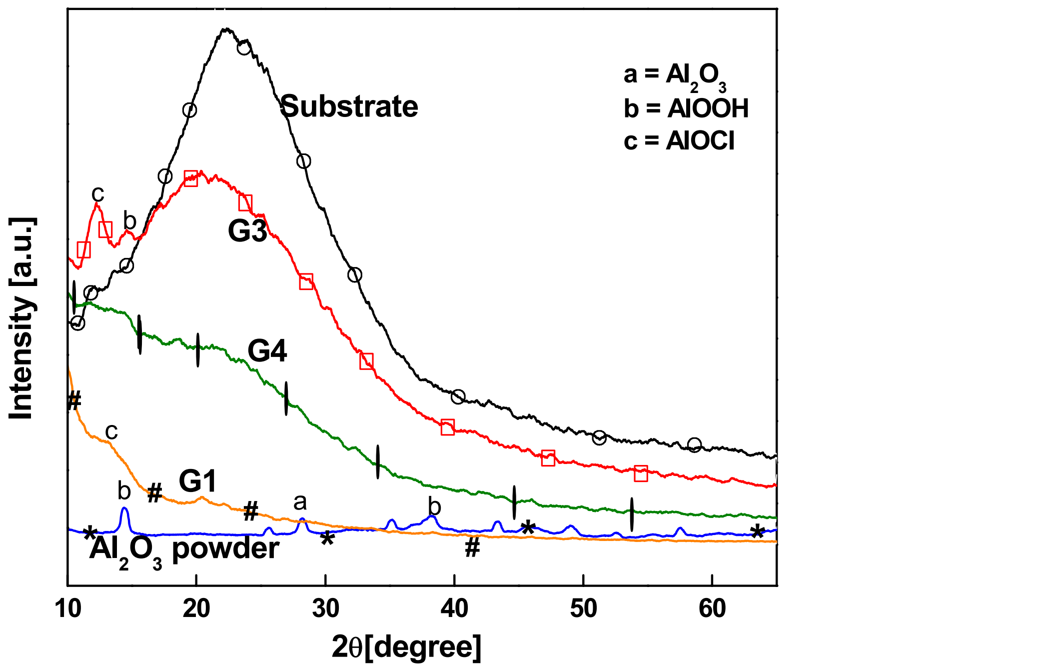

Fig. 1 – XRD patterns of alumina films deposited on microglass substrates by SPD.

The XRD measurements of all the samples showed a typical pattern of an amorphous alumina, without any clear indication of crystallinity. In G1 and G3 samples, deposited at lower temperature (220^{o}C), the presence of crystalline AlOCl and/or AlOOH phases is observed. Even so, the predominant phase is amorphous Al_2O_3. These results are according to the literature.[12]

c) The influence of deposition parameters on the surface morphology

The surface morphology of alumina films deposited at different temperatures (T = 220-320 ^{o}C) and using different number of spraying sequences (30, 55), are presented in Figure 2. The addition of organic additives, such as AcAc, in the precursor solutions can be a tool in tailoring alumina thin films morphology, in order to obtain porous films.[11] This films can be further infiltrated with metal or/and metal oxide particles for the preparation of a cermet, used as solar-thermal selective absorber, the main component in a solar flat-plate collector. Depending on the variation of the deposition parameters, different surface morphologies are observed for studied samples.

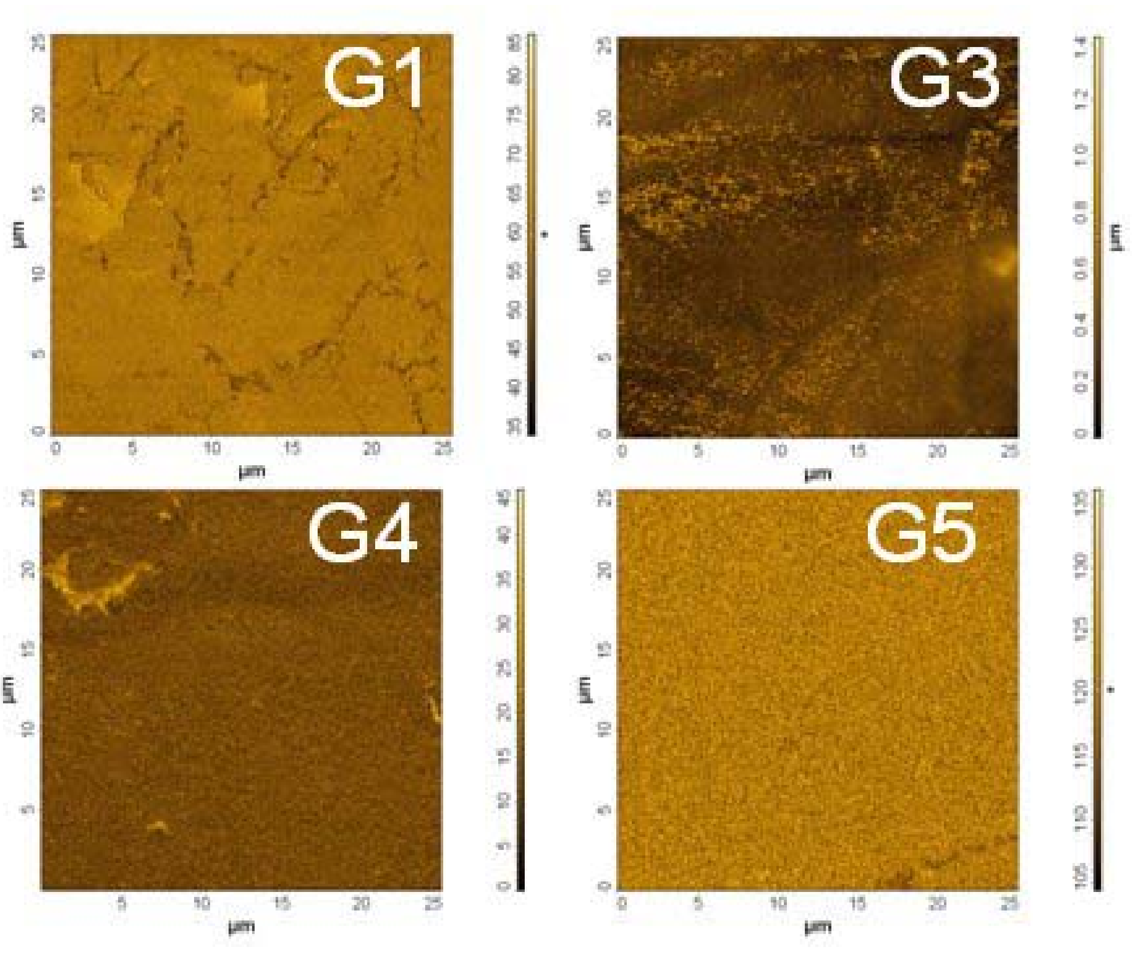

Fig. 2 – 2D AFM images of samples G1, G3, G4 and G5 obtained by SPD.

The surface roughness of sample G1, deposited at lower spraying sequence (30), is higher (192nm) comparing to those of sample G3 (135 nm) deposited at n_{sp}= 55, confirming the film densification. The roughness of the Al_2O_3 films depends on the thickness and deposition temperature. At the same spraying sequence number (n_{sp}=55), the higher roughness (135 nm) is found for the thicker Al_2O_3 layer deposited at 220 ^{0}C (sample G4), probably due to the film composition: amorphous Al_2O_3 and amorphous and/or crystalline by-products (*e.g.* crystalline AlOCl). The general trend is a decrease of the films roughness with the temperature increase; the sample prepared at 320ºC (G5) has the smallest roughness (26 nm).

The inhomogeneous film G1, with cracks, is not suitable for the cermets' development. The films obtained at higher temperatures using a large number of spraying sequences are smooth and have a homogeneous surface aspect.

CONCLUSIONS

The alumina thin films obtained from $AlCl_3 \cdot 6H_2O$ dissolved in aqua-ethanol solution via spray pyrolysis deposition have been studied as a function of deposition parameters (substrate temperature, annealing and spraying sequence number). The experimental results have been shown that the solar absorbtance is improved by annealing, higher deposition temperature and higher spraying sequence number. These conditions favour the by-product elimination by increasing the alumina content in the sample. The thermal emittance values are higher (ε>0.1), but further infiltration with metal particles is expected to strongly decreases the ε values.

At deposition conditions, the samples contain amorphous Al_2O_3 phase. The Al_2O_3 film roughness decreases with temperature increase; at higher temperature, re-arrangements in the films occurs thus the film homogeneity are improved.

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