Nanocomposite dodecyl sulfate-modified Mg-Al layered double hydroxide thin films deposited via laser technique

A. Vlad*, R. Birjega*, A. Matei*, I. Tirca*, M. Dinescu*, R. Zavoianu**, O.D. Pavel**, M.C. Corobea***

* National Institute for Lasers, Plasma and Radiation Physics, Atomistilor 409, Bucharest, Romania, angela.vlad@inflpr.ro

** University of Bucharest, Faculty of Chemistry, Department of Chemical Technology and Catalysis, 4-12 Regina Elisabeta Bd., Bucharest, 030018, Romania,

***National R.&S. Institute for Chemistry and Petrochemistry, ICECHIM, 202 Splaiul Independentei Str., CP-35-274, 060021, Bucharest, Romania

ABSTRACT

Nowadays, there is an interest in using nanomaterials such as layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, as potential nanocontainers of corrosion inhibitors in self-healing corrosion protection coatings. The aim of this work is to investigate the properties of these composite functional materials obtained as thin films by pulsed laser deposition (PLD). LDH based on Mg-Al (Mg/Al atomic ratio of 2.5) was used as host material, while dodecyl sulfate (DS) acted as organic surfactant guest material. The films were deposited by PLD technique using a Nd:YAG laser working at different wavelengths (266 nm, 532 nm and 1064 nm), and having a 10 Hz pulse repetition rate.

The results evidenced the ability of PLD to produce composite LDHs films intercalated with an organic surfactant (DS), with prospects to act as corrosion protective coatings.

Keywords: laser ablation, nanocomposites, hydrotalcites, dodecyl sulfate

1 INTRODUCTION

Layered double hydroxides having a brucite-like structure are a class of host-guest materials, which can be described by the formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2](A^{n-})_{x/n}\bullet mH_2O$, where M^{2+} and M^{3+} are divalent (Mg, Ni, Zn, Cu or Co) and trivalent (Al, Cr, Fe, or Ga) metal ions, respectively[1]. A^{n-} is an exchangeable anion, or an organic anion, compensating the positive charge of the hydroxide layers. Functional materials can be produced by introducing anions with specific functions in the LDH structure [2-4]. LDHs have been studied extensively due to their low cost of production and capacity to intercalate organic anions into the interlayer space, as a result of their high anionic exchange ability [4-5]. Early works on the deposition of LDH thin films were by evaporation deposition and in situ growth method or by substrate-induced growth technique. Herein, we report the deposition of films of dodecyl sulfate-modified Mg-Al layered double hydroxides by PLD. Pulsed laser deposition has gained worldwide acknowledgement as a reliable and inexpensive method for obtaining thin films of simple or complex compounds [7]. The targets used in the deposition are the organo-LDH composites accommodating the organic dodecyl sulfate guest molecule. The composite organo-LDH powders were prepared similarly as the pristine Mg-Al-LDH ones. The targets used for PLD were pressed pellets synthesized from these powders. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to investigate the topography of the thin films. The degree of crystallinity of the powders and films was checked by X-ray diffraction, while spectral techniques (FT-IR, UV-VIS) were used to evidence the interlayer composition, in particular of the organic component for both powders and thin films. There are several ways to intercalate organic anions into the galleries of LDHs: co-precipitation in the presence of organic species, ion exchange and reconstruction through the 'memory effect'. Two procedures were carried out for the synthesis of MgAl-LDHs with co-intercalated DS guests: the intercalation of dodecyl sulfate either by co-precipitation or reconstruction.

2 EXPERIMENTAL

2.1 Powders

The chemicals used for the preparation of the MgAl-LDHs and dodecyl sulfate-modified LDHs were commercially available raw materials of the highest purity.

MgAl-LDH. The MgAl-LDH powders with molar ratio Mg/Al=2.5 were prepared via coprecipatation at 40 °C under low supersaturation conditions, pH of 9.5-10. The powders were prepared from the following materials: $Mg(NO_3)_2\bullet 6H_2O$, $Al(NO_3)_3\bullet 9H_2O$, anhydrous $NaCO_3$ and NaOH. We denote this powder Mg2.5Al.

DS-MgAl-LDH. The dodecyl sulfate-modified LDH powders were prepared by direct coprecipitation and

reconstruction, respectively. The materials that were employed in the coprecipitation procedure were Mg2.5Al(OH)7(DS).2,5H_2O,Mg$(NO_3)_2$.6H_2O,Al(NO_3)3•9 H_2O, NaOH, NaDS, and sodium dodecyl sulfate (SDS=$NaCl_{12}H_{25}SO_4$, molar ratio DS/Al=1.5). The final powder, labeled PMg2.5Al-DS, was obtained following the same procedure as for the Mg2.5Al powder. The reconstruction via DS intercalation into the LDH was carried out by immersing the mixed oxide powder derived from the gentle calcination (18 h at 460° C in air flow) of the Mg2.5Al powder in an aqueous solution of DS (molar ratio SDS/Al=1.5). The immersion occurred at room temperature for 24 h. The recovered solid powder was labeled RMg2.5Al-DS.

The obtained powders were studied by X-ray diffraction (XRD) using a PANalytical X'Pert MPD system (λCuKα=1.5418 Å), and by Fourier transform infrared spectroscopy (FTIR) with the aid of a JASCO FTIR 6300 spectrometer.

2.2 Thin films

Pulsed laser deposition is a contact free technique, which allows the obtaining of thin films with good adherence, controlled thickness, structural and morphological properties, along with the preservation of target stoichiometry and purity. There are a limited number of reports on the formation of oriented films. Our group recently report on the successful deposition of LDHs and their derived oxides thin films by laser techniques: pulsed laser deposition (PLD) and matrix assisted pulsed laser evaporation (MAPLE) [8-12]. The thin films were obtained using as ablation source a Nd:YAG laser emitting at different wavelengths (266, 532 and 1064 nm), and having a pulse repetition rate of 10 Hz. The PLD films were deposited at room temperature on flat silicon and quartz substrates following 20,000 pulses using a laser fluence of 2 J/cm^2.

The targets to be used in PLD experiments were dry pressed pellets obtained from the prepared Mg2.5Al, PMg2.5Al-DS and RMg2.5Al-DS powders.

The XRD patterns were collected using grazing incidence (GI) geometry, at an angle of 0.25°. Their FTIR spectra were recorded with a JASCO 6300 spectrometer. The surface morphology of thin films was examined by atomic force microscopy (AFM), using a Park XE-100 system in non-contact mode.

3 RESULTS AND DISCUSSIONS

3.1 Powders

The SEM images (Fig.1) of the as-prepared powders reveal a difference in the morphology of organo-modified LDH samples.

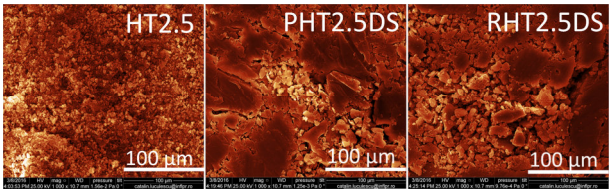

Fig. 1. SEM images of prepared powders

The XRD patterns (Fig. 2 and Table 1) and thermal analysis confirms the DS interlayer intercalation.

Powder samples	Phase comp.	Structural data					
		a (nm)	c (nm)	IS (nm)	D_{001} (nm)	D_{110} (nm)	Tilt angle
Mg2.5Al	LDH phase	0.305	2.288	0.28	16	37	-
PMg2.5Al-DS	DS-LDH phase	0.304	7.8767	2.14	8	37	90
RMg2.5Al-DS	Dominant DS-LDH	0.304	7.462	2.01	11	13	75

Table 1 The phase composition and the structural data of obtained powders are presented.

There are no major differences between co-precipitation and reconstruction method, except for a larger amount of organic material deposited on the external layered LDH crystallites, which is observable from the difference in intensities of the hydrocarbon chain scattering peaks marked by a rectangle in Fig. 2 [2].

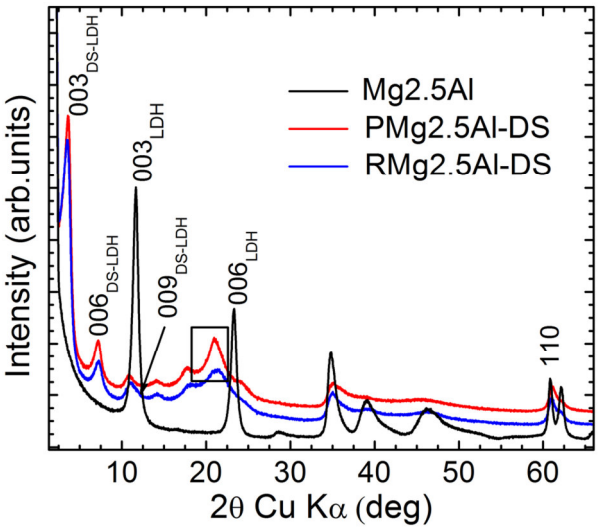

Fig. 2 The XRD patterns of the powders.

The results are consistent with the thermal analysis and FTIR data (not shown here).

3.2 Thin films

The formation of oriented films (only the basal reflections are observable) using all 3 laser harmonics to ablate the pristine Mg2.5Al target is validated by the GI-XRD patterns (Fig. 3).

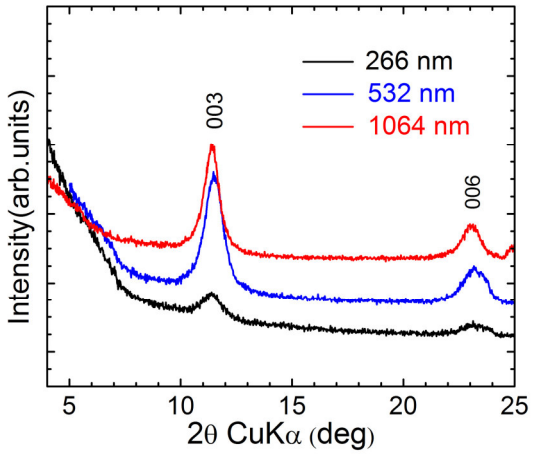

Fig. 3 The XRD pattern of thin films grown by PLD at different ablation wavelengths.

Less organized structures are formed following ablation at 266 nm laser wavelength. The XRD patterns of the films deposited form the DS-modified LDH targets exhibit poorly defined peaks, irrespective of the used ablation wavelengths, stating for the formation of less oriented structures and the partial delamination of the LDHs. The result is endorsed by thermal analysis, which showed a high thermal stability of the Mg2.5Al powder in comparison with the PMg2.5Al-DS and RMg2.5Al-DS ones, respectively.

The morphology of the Mg2.5Al thin films deposited at different wavelengths depicted in Fig. 4 reveals a rough surface with big grains onto the surface.

AFM analysis proved to be very difficult for the PMg2.5Al-DS and RMg2.5Al-DS samples. We encountered difficulties such as unstable feedback, tip alteration during scanning. These difficulties were attributed to the relatively high roughness of the respective surfaces, together with the fact that the grains / particles which make up the deposited material are held together by relatively weak forces.

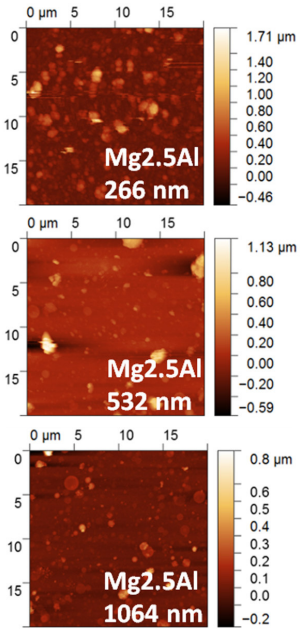

Fig. 4 AFM images of Mg2.5Al thin films deposited by PLD at three different ablation wavelengths (20x20 µm).

The FTIR data (not shown here) has confirmed, for all targets and wavelengths, that the transferred films have the same structure as their respective target. In particular, the CH_2 stretching bands, as well as symmetric vibrations of S=O characteristic for DS, are clearly visible. Peaks assigned to carbonate counterions are also visible, standing for partial intercalation of the DS counterion or for a delamination of layered structures when exposed to air.

4 CONCLUSIONS

PLD proves to be a suitable technique for deposition of complex structure such as LDHs or organo-modified LDHs (DS-LDHs). The transfer of pristine LDH and intercalated DS-LDHs occurred for all the three selected wavelenghts 266, 532 and 1064 nm of Nd:YAG laser with the conservation of the organic anion in the interlayer space.

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