Influence of solvents on properties of solar selective coatings obtained by spray pyrolysis

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Abstract. Solar selective coatings for solar thermal flat-plate collectors consisting of crystalline copper oxides and amorphous nickel oxide composites were obtained by robotic spray pyrolyzed deposition. The parameters were optimized for increased spectral selectivity (S): high solar absorptance and low thermal emittance. The coatings were deposited using nickel and copper acetate, dissolved in mixed solvents with various water: ethanol ratios. The coatings' properties were characterized in terms of crystalline composition (XRD), surface morphology (AFM, contact angle) and optical properties (solar absorptance, thermal emittance and spectral selectivity). Considering the precursor solutions composition (solvent, wetting behaviour), the growth processes were modelled for two different systems: predominant hydrophilic and predominant hydrophobic. The high selectivity values ($S > 30$) of the optimized composite coatings were explained based on two parallel mechanisms: intrinsic absorption and multiple reflections generated when absorbers with controlled roughness are deposited.

Keywords. Spray pyrolysis deposition; surface engineering; solar selective coatings.

1. Introduction

The active component in a solar thermal collector is the absorber plate which strongly influences the solar thermal conversion. Its role is to convert the incident solar radiation into heat, without significant heat losses (due to thermal radiation). Therefore, the absorber coating must have high solar absorption ($\alpha_s > 0.92$) in the visible wavelength range (0.29–2.5 μm) and low thermal emittance ($\varepsilon_T < 0.15$) in the infrared spectral domain ($\lambda > 2.5 \mu\text{m}$) (Carlsson 2007). The ratio α_s/ε_T defines the spectral selectivity (Duffie and Beckman 2006).

The selective coatings evolved from the electrochemically deposited black chromium (Bayati *et al* 2005) or nickel-pigmented alumina (Boström *et al* 2008; Zemanová *et al* 2008) to the coatings obtained by physical vapour deposition (PVD) (Nunes *et al* 2003) or chemical vapour deposition (CVD) (Oelhafen and Schüler 2005) which are mainly based on titanium oxynitride. These advanced coatings show good optical properties; however, the deposition processes require complex and high cost equipment and provide a rather poor ecological balance and energy pay-back time.

Spray pyrolysis deposition (SPD) involves standard equipment, a small amount of chemicals which leads to non-toxic byproducts, and is up-scalable for industrial applications, allowing large deposition surfaces (OjaAcik *et al* 2009).

Nickel and copper oxide are widely used as multifunctional materials due to their good chemical stability, along with suitable electrical, electrochemical and optical properties. They have numerous applications ranging from electrochromic display devices (Valyukh *et al* 2010), sensors (Hongbing *et al* 2010), batteries (Souza *et al* 2006) to solar absorbers (Isac *et al* 2007). The use of single layer of black copper/nickel films based on copper oxides and nickel oxides for solar coatings was reported earlier (Voinea *et al* 2009). Statistic composites consisting of CuO_x and NiO_x are less studied, although increased spectral selectivity could be expected in this case.

The coatings surface morphology and roughness plays an important role in improving the absorber efficiency; textured/rough surface can favour multiple internal reflections leading to increased values of solar absorption. By using SPD, the films' morphology can be technologically controlled through the deposition parameters and precursor solution properties. The surface tension of the liquid influences the droplets formation and the wetting behaviour on the substrate and thus, the grain size and films' characteristics (surface roughness).

The paper focuses on the preparation of statistic composites, based on nickel and copper oxides with controlled optical and surface properties, to be used as selective coatings. The films were deposited from aqueous–alcoholic precursor solutions onto copper substrates by robotic spray pyrolysis. The influence of alcohol (ethanol) concentration on thin film formation mechanism and properties of films was investigated.

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2. Experimental

2.1 Solar absorbers deposition

Copper oxides and nickel oxides mixed films (samples A0–A5) were deposited on copper substrate (50 × 50 mm, Beofon), at 330 °C, by robotic spray pyrolysis, from a previously optimized receipt (Voinea *et al* 2009) for single layer deposition. The technological parameters were previously optimized in order to obtain an optimum thickness of the layers (800 nm) considering the application and functional key parameter: spectral selectivity.

The substrate was mechanically polished and then washed with bidistilled water. A mixture of nickel acetate, 0.2 M and copper acetate, 0.1 M (reagent grade, Scharlau), dissolved in water (W) and ethanol (Et), with alcohol concen-

tration varying from 0 to 40 %, was used, as presented in table 1.

2.2 Solar absorbers characterization

The crystalline composition was assessed using a Bruker D8 Discover Advanced Diffractometer using CuK α radiation source ($\lambda = 1.5406 \cdot 10^{-10}$ m), in the range of $2\theta = 2-80^\circ$. The surface morphology was evaluated by Atomic Force Microscope (AFM, NT-MDT model BL222RNTE). The images were taken in a semi-contact mode with Si-tips (NSG10, force constant 0.15 N/m, tip radius, 10 nm).

Static contact angle measurements for clean copper substrate and for the A0–A5 samples were performed with the sessile drop method, using an OCA-20 Contact Angle-meter

Table 1. Precursor solution properties.

Sample	A0	A1	A2	A3	A4	A5
Solvent, Et%	0	2.5	5	10	20	40
$\sigma_{p.s.}$ (mN/m)*	72.4	65	58.9	52.2	41.1	31.2
θ_{Cu} (degree)**	73.5	73	69	67	55	40

* $\sigma_{p.s.}$ is the precursor solution surface tension;

** θ_{Cu} represents contact angle measured for clean copper substrate and precursor solution.

Table 2. Crystallite size dimensions.

Sample	Solvent % Et*	d_{CuO} [nm]	d_{Cu_2O} [nm]
A0	0	6.7	7.4
A1	2.5	10.5	4.9
A2	5	5.56	4.4
A3	10	14.9	6.5
A4	20	14.9	6.5
A5	40	10	8.6

Figure 1. XRD patterns of films.

(DataPhysics Instruments). A drop (5 μL) of liquid—water or precursors solution—was placed, with 1 $\mu\text{L/s}$ velocity, on the film's surface.

Optical absorption measurements were carried out with a UV-Vis Spectrophotometer (Perkin Elmer Lambda 25) and a FTIR Spectrophotometer (BXII Perkin Elmer). The solar

Figure 2. a–f. AFM image of sample obtained from precursor solutions with different alcohol concentrations: sample A0, 0% Et (a), A1, 2.5% Et (b), A2–5 % Et (c), A3–10% Et (d), A4–20% Et (e) and A5–40% Et (f).

absorbance and thermal emittance were calculated from the reflectance spectra.

3. Results and discussion

X-ray diffractograms of the samples obtained from aqueous and aqueous–ethanol solutions are presented in figure 1. Specific diffraction lines corresponding to CuO (tenorite, PDF 00-003-0884) and Cu₂O (cuprite, PDF 00-003-0892) crystalline phases, together with Cu (PDF 01-071-3761) substrate, are identified. According to XRD patterns, no diffraction peaks for crystalline nickel oxides are observed. Based on preliminary studies for nickel ion identification and considering XRD diffraction patterns, at the deposition temperature, the nickel oxides are considered to be amorphous phases (Souza *et al* 2006).

The average crystallite sizes were calculated using the Scherrer formula (table 2). The solvent composition in the precursor solutions has no significant effect on the crystalline composition in thin films; the ethanol addition generally leads to the increase of the Cu₂O average crystallite sizes and to a non-uniform variation of CuO average crystallite sizes. These variations have an influence on the films growth mechanism.

In developing a material for an efficient solar thermal absorber, the surface morphology is essential. Using atomic force microscopy, the sample morphologies were investigated and they are presented in figures 2a–f.

The AFM images show different surface morphologies, significantly depending on the ethanol content in the precursor solution. The sample A0 (no ethanol addition) has a rather uniform, spherical morphology (figure 2a). As the concentration of alcohol increases, growth of the specified grains is promoted and aggregates are formed from

Figure 3. Variation of surface average roughness with ethanol content.

Table 3. Correlation of surface properties with spectral selectivity.

Sample	Solvent % Et*	θ_w [degree]	α_s	ε_T	S
A0	0	52.5	0.915	0.030	30.5
A1	2.5	51.0	0.917	0.030	30.6
A2	5	38.5	0.919	0.075	12.3
A3	10	30.2	0.917	0.034	27
A4	20	20.0	0.917	0.030	30.6
A5	40	13.5	0.911	0.025	36.4

*Percentage (in volume) of ethanol in water–ethanol precursors solution.

smaller crystallites/grains which merged into larger ones (figures 2b–f). The consequence is aggregates sharpening and shallow cavities forming a phenomenon being known as “Ostwald ripening” (Validžić *et al* 2008). Following this mechanism, the surface roughness is also increasing with ethanol concentration in the precursor solution.

In the systems containing ethanol, a linear increase of the surface average roughness with ethanol content is registered, supporting the idea of a change in the nucleation/growth mechanism as a result of ethanol addition (figure 3). Considering the polarity difference between water and ethanol, the data suggest that there is a significant change in the cation (copper, nickel) hydration, thus in their reactivity.

Contact angle (CA) measurement is a simple and low cost method to assess the surface properties of a thin film, mainly the surface roughness/porosity, surface energy and wettability (Voinea *et al* 2008). Especially for solar absorbers, the wettability is very important: the final absorber surface must be hydrophobic (thus high contact angle measured for water, $>90^\circ$), while the intermediate layers in the case of multi-layer absorbers should be hydrophilic for water based precursors (with contact angle values lower than 90°).

The initial values of the contact angle measured for water range between 52.5 and 13.5 (table 3), indicating the formation of the hydrophilic surface required for a further deposition of the anti-reflective layer. There is a good correlation between surface roughness (S_a) and initial values of CA. As the samples have almost the same crystalline composition, CA values are rather influenced by the surface roughness. Thus, it is likely that the enhancement of the surface hydrophilic properties could be realized by adequately increasing the surface roughness.

It also has to be mentioned that the contact angle decrease has an opposite trend compared to roughness, but there is not a linear dependence; therefore, we may recommend contact angle measurements only as a preliminary and rough step in evaluating surface morphology evaluation.

An efficient solar selective coating has the solar absorption coefficient, $\alpha_s > 0.92$ and thermal emittance, $\varepsilon_T < 0.15$ (Carlsson 2007). The absorbers reported in this paper have a very good spectral selectivity, as the data presented in table 3 show. The high solar absorption values can

be explained by the following mechanisms (Bayati *et al* 2010):

- intrinsic absorption or normal absorption; when light propagates through a medium that is not vacuum, it attenuates, which is a fundamental property for a solar coating;
- multiple reflection/absorption: when rough absorbers are used, the waves are subjected to multiple reflection into the narrow(er) pores of the layer and the waves' energy is partially absorbed into the material for each contact, leading to an increased solar absorptivity.

3.1 Growth mechanism

During the spray pyrolysis, small droplets are formed from the precursor solutions. The metal acetate molecules are thermally cracked, and several reactions occur like dehydration ((1) and (2)) followed by decomposition ((3) and (4)), leading to nucleation and thin film growth.

During SPD, droplets size in the aerosol has an important role in film formation. The droplets diameter is directly influenced by the precursor solution surface tension; the direct proportionality between the pressure difference (internal and external droplet pressure) and the surface tension is given by the well-known Young–Laplace equation. Thus, decreasing the surface tension (by adding ethanol) results in lower internal pressures and/or in the possibility of getting lower sized droplets. This can explain the roughness increase while developing larger aggregates. Supplementarily, the contact angles were measured for each precursor solution in contact with clean copper substrate (table 1) which show an increased wetting behaviour of the precursor solution with increasing alcohol concentration.

Alcohols are known to reduce the surface tension of the water based solutions. The precursor drops will generate a less isolated nucleation centre due to the formation of large particles which tend to coalesce, for reducing their surface energy. Further, particle growth might be a result of continuing nucleation in the film on the substrate, and Ostwald ripening type of growth will lead to the formation of large oriented aggregates (Singh *et al* 2007).

Based on the Murakami *et al* (2007) mechanism, the film growth was modelled (figure 4) considering: (a) nucleation and (b) thin film growth and/or coalescence

Figure 4. Mechanism proposed for films deposition by SPD from precursor solutions with: (a) high contact angle and (b) low contact angle, measured on copper substrate.

growth. Two different precursors were considered: solutions with good wetting behaviour—as in the case of alcoholic precursor solutions—and average wetting solutions. First, isolated nuclei are formed on the heated substrate. In the case of films obtained from solutions with higher alcohol content, thus low contact angle, the number of isolated nuclei is rather small and the growth rate is predominant. The grains can further coalesce to form larger aggregates. Therefore, the grain size and also the surface roughness increases. In this case, particle growth might be a result of an Ostwald ripening growth type and it can occur mainly through solid-state diffusion. For the solutions with low wetting behaviour, the particle growth is mainly due to continuous nucleation with the formation of rather small spherical particles (figure 4).

4. Conclusions

Selective coating based on copper and nickel oxides statistic composites with controlled optical and surface properties were deposited from aqueous–alcoholic mixed precursor solutions onto copper substrates, by robotic spray pyrolysis. The method involves a small amount of chemicals which leads to non-toxic byproducts and can be used in industrial applications.

The alcohol percentage is modifying the surface tension of the precursor solution which influences the droplets formation and thus the film characteristics (surface roughness).

The solar absorbers have high selectivity values ($S > 30$) as a result of the intrinsic absorption due to the presence of copper and nickel oxides, and due to multiple reflections generated when rough enough absorbers are used. The best selectivity (36.4) is registered for thin films with highest roughness, obtained from precursors with 40% ethanol, in the water–ethanol mixed solvent.

Based on the main precursor characteristics and morphology studies, a growth mechanism is proposed for two different precursor solutions: with good wetting behaviour as in the case of alcoholic precursor solutions and with average wetting solutions.

Modifying the alcohol concentration in the precursor solutions and the wetting behaviour of the precursor solution represents an efficient path to change growth processes of thin film, especially the surface properties

(surface roughness) and, consequently the absorber's spectral selectivity.

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