

Tailoring Alumina Matrix Optical Properties for Colored Solar Thermal Absorber Coatings

Luminita Isac, Dana Perniu and Anca Duta

Renewable Energy Systems and Recycling Research Center, Transilvania University of Brasov,
Brasov, Romania

Abstract

The absorber plate is the key component in a flat plate solar thermal collector. Most of the black and some of the colored absorber coatings are based on cermets, composed of metals or inorganic pigments embedded in a ceramic matrix of metal oxides, such as alumina (Al_2O_3).

The current work describes the optimization steps of the alumina matrix to get optical properties and morphology suitable for the pigment layers infiltration to develop efficient colored (yellow and green) solar absorber coatings/plates. The alumina matrices were obtained by the depositing the alumina layer on the Al substrate using two different methods: immersion and robotic spraying of a diluted sol. The optimized alumina matrix, obtained by immersing the Al substrate in a diluted alumina sol (Al_2O_3 sol: $\text{H}_2\text{O} = 1: 9$) for 24 hours, has a porous morphology and promising optical properties: $\alpha = 0.16$, $\varepsilon = 0.06$.

Keywords: solar thermal collectors, absorber coatings, alumina matrix, robotic spraying deposition, optical properties

1. Introduction

The main challenges faced in the research on solar thermal collectors are focused on enhancing the thermal performance, increasing the reliability and the long-term performance stability (Fernandes et al., 2017). Additionally, a solar thermal collector must be economically feasible, thus should have a low cost, that means not only low cost materials, technologies and component parts but also a long service lifetime (Sun et al., 2014). Besides increasing the efficiency and durability, the architectural acceptance of the solar thermal collectors currently represents an important research topic, colored solar thermal collectors being aesthetically preferred to the standard black or dark-blue ones, although their thermal efficiency is expected to be lower. Therefore, new, affordable and efficient solutions are expected, supporting the integration of the solar thermal systems on the building's facades, according to their design specifications, mainly related to architectural acceptance and good conversion efficiency. Recently, Visa et al (2017) reported the development of a trapezoidal solar thermal collector, with 0.67 m^2 active area and 69.42% nominal efficiency, which can be used as a building block in arrays with various surfaces, shapes and colours.

The active component in a solar thermal collector is the absorber plate, usually coated with a black or dark blue layer to absorb as much solar radiation as possible and convert it into thermal energy. This energy is further transferred to the working fluid, thus the absorber plates must possess good thermal and radiative properties (Alami and Aokal, 2018). Solar selective absorber (SSA) coatings are designed using materials with carefully engineered optical properties: high solar absorptance ($\alpha > 0.9$) over the solar spectrum and low thermal emittance ($\varepsilon < 0.1$) in the IR region, at the operating temperature, along with thermal and mechanical resistance. Cost-effective and environmentally friendly production processes represents additional requirements for SSA coatings. In this context, spray pyrolysis (SP) and sol-gel (SG) are relatively simple and industrial up-scalable techniques that are considered suitable for manufacturing SSA coatings (Isac et al., 2018).

The most frequently developed industrial solar selective absorbers are based on metal-dielectric composites also called cermets, mainly consisting of nanoscale metal particles (Ni, Au, Co, Mo, Cr) or inorganic pigment particles (Fe_2O_3 , CuS, V_2O_5) embedded in a dielectric, ceramic matrix (Céspedes et al., 2014, Duta et al., 2014,

Estrella-Gutiérrez et al., 2016, Purghel et al., 2008). Cermet based SSA coatings with good solar selectivity, even at high temperatures, have been already successfully commercialized (Bermel et al., 2012).

Among cermet composite coatings, SSA coatings with alumina (Al_2O_3) matrix have been widely used as selective solar absorber surfaces with good optical properties (low thermal emittance, $\epsilon < 0.1$) and thermal stability, due to the possibility of tailoring the coating's surface aspect to obtain a porous morphology, suitable for further metal/pigment particles infiltration. Alumina is a dielectric material with excellent properties, such as high thermal and chemical stability, high hardness, high refractive index ($n = 1.61 - 1.75$), low permeability of alkali ions and high radiation resistance (Balakrishnan et al., 2013, Khatibani and Rozati, 2015). Amorphous and/or crystalline alumina thin films with good adhesion on different substrates (Al, Cu, stainless steel) are considered promising materials acting as ceramic matrix in solar selective absorber coatings.

This work focuses on the development and optimization of the alumina matrix ($\text{Al}/\text{Al}_2\text{O}_3$) obtained by the deposition of alumina layer on the aluminium substrate using two simple and low-cost techniques: the immersion in diluted alumina sol and robotic spraying, at average temperature ($T = 130\text{ }^\circ\text{C}$), of a diluted alumina sol. The optical properties (α , ϵ) of the alumina matrix were correlated with the chemical composition (XRD and EDX), crystalline structure (XRD) and morphology (SEM).

2. Experimental

In developing the colored absorber coatings, before the infiltration with pigment particles, the Al substrate and alumina matrix are necessary to be optimized, using the spectral selectivity (S) as output property.

The Al substrates (3cm x 3cm samples) were chemically pre-treated in three steps:

- Degreasing in ethanol (98%, ChimReactiv) and conditioning the commercial Al substrates (99,5% Beofon, thickness 1 mm) in 4% NaOH solution (NaOH 99%, Scharlau Chemie);
- Immersing the alkali treated aluminium substrates in HNO_3 (HNO_3 65%, Chimopar) solution, at different acid concentrations: 0.5M, 0.75M and 1M, for 0.5 h, 3h and 20 h;
- Neutralizing the residual acid on the aluminum substrates by immersing in 2% Na_2CO_3 solution (Na_2CO_3 99.9%, Scharlau Chemie) for 10 minutes, followed by rinsing with distilled water and drying in compressed air flow.

The alumina matrix represents an additional layer of Al_2O_3 deposited on the pre-treated Al substrate (nominated as **A**) that was obtained using two different deposition techniques:

- Immersion of the Al substrates in a diluted alumina sol (Al_2O_3 : $\text{H}_2\text{O} = 1: 9$ in volumes) for 24, 48 or 72 hours; the samples were nominated as **A/AOSG24**, **A/AOSG48** and **A/AOSG72**;
- Robotic spraying, at $T = 130\text{ }^\circ\text{C}$, of a diluted sol (1:9) using 5, 10 or 15 spraying sequences; the samples were nominated as **A/AOSGs5**, **A/AOSGs10** and **A/AOSGs15**.

The alumina sol was prepared using the sol-gel technique, according to Milea et al. (2013): aluminium chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 98%, Scharlau Chemie) was added in a mixture of bi-distilled water and absolute ethanol (1:1) under continuous stirring, at room temperature ($25\text{ }^\circ\text{C}$), to promote the hydrolysis and condensation processes; after 10 minutes, 5.5 millilitres of polyethylene glycol (PEG 400, synthesis grade, Scharlau Chemie) was gradually added (0.5 millilitres/minute) under continuing stirring; the resulted sol was left for ageing 5 days. Afterwards, the sol was diluted and used as precursor for the Al_2O_3 deposition on the chemically pre-treated Al substrate **A**.

The optical properties of the Al substrates and alumina matrices (ϵ , α) were evaluated using Fourier Transform Infrared spectroscopy (FTIR, Bruker Vertex 70, equipped with a integrated sphere coated with gold) and UV-VIS-NIR spectrophotometry (UV-VIS-NIR Spectrophotometer Perkin Elmer, double-beam spectrophotometer, equipped with integrating sphere to 150 mm).

The thermal emittance, ϵ , was calculated from the reflectance spectra recorded in the IR domain ($\lambda = 2.5\text{-}20\text{ }\mu\text{m}$), as the weighted fraction between the absorbed energy and the Planck blackbody energy (I_p) at certain wavelength (λ) and temperature (T , ambient temperature in this work), using eq. (1) (Duta et al., 2014):

$$\epsilon = \frac{\int_{2.5}^{20} I_p(\lambda)(1-R(\lambda,T))d\lambda}{\int_{2.5}^{20} I_p(\lambda,T)d(\lambda)} \quad (1)$$

The solar absorptance (α) was calculate using eq. (2) (Duta et al., 2014) from the reflectance spectra recorded in the UV-VIS-NIR domain ($\lambda = 0.28-2.5 \mu\text{m}$):

$$\alpha = \frac{\int_{0.28}^{2.5} I_{\text{sol}}(\lambda)(1-R(\lambda))d\lambda}{\int_{0.28}^{2.5} I_{\text{sol}}(\lambda)d(\lambda)} \quad (2)$$

where: $R(\lambda)$ is the material's reflectance and I_{sol} is the solar irradiance (ISO 9854-1, 1992) with an air mass of 1.5.

The ratio of the two important optical parameters, solar absorptance (α) and thermal emittance (ϵ), gives the spectral selectivity, S , which generally characterizes the optical performance of an absorber material. Spectral selectivity is defined as the ability of a material to ideally behave as a black body, absorbing the maximum of the incoming solar radiation and minimizing energy losses through infrared radiation (Isac et al., 2017).

The overall crystallinity degree (estimated using the device software EVA 1.4) and the composition of the crystalline phases in the samples were evaluated by X-Ray Diffraction (XRD, Bruker D8 Discover Diffractometer with $\text{Cu}_{K\alpha 1}$ line) using the locked-couple technique in the 2θ range from 20° to 70° . The crystalline phase composition (weight %) was obtained using the integration of the diffraction data (calculating the area, S , under the diffraction peak by mathematical integration) and then eq. (3) was applied (Birkholz, 2005):

$$A(\%) = \frac{\sum_i^n S_{i(A)}}{\sum_i^n S_{i(A)} + \sum_j^m S_{j(B)} + \dots} \times 100 \quad (3)$$

where $S_{i(A)}$, $S_{j(B)}$ are the estimated peaks areas for the individual crystalline phases A, B.

The surface morphology of the alumina substrate and of the alumina matrix was investigated using Scanning Electron Microscope (SEM 3500N, Hitachi). The surface elemental composition of the samples was identified using an energy dispersive spectrometer (EDS), mounted on the SEM.

3. Results and discussions

3.1. The Al substrate optimization

The influence of the HNO_3 solution concentration and of the immersion duration on the optical properties (thermal emittance, preferably $\epsilon < 0.2$) of the aluminium substrates was investigated and the results are presented in Table 1. Based on the experimental values, the aluminium substrates with lowest thermal emittance ($\epsilon = 0.22... 0.26$) were further investigated by UV-VIS-NIR spectrometry and the results show that the solar absorptance has similar values: $0.12...0.13$.

Tab. 1: The thermal emittance values for chemically pre-treated Al substrates in HNO_3 solution with different concentrations, at different immersion times

Optical property		ϵ		
HNO ₃ concentration [moles/L]		0.5	0.75	1
Immersion time [h]	0.5	0.36...0.45	0.35...0.42	0.35...0.40
	3	0.25...0.42	0.24...0.36	0.21...0.36
	20	0.22...0.31	0.22...0.26	0.17...0.32

The chemically treated substrate with the best spectral selectivity ($S = 0.59$), having $\alpha = 0.13$, $\epsilon = 0.22$ was obtained by immersion in 0.75M HNO_3 solution for 20 hours and was nominated as **A**.

According to the X-Ray diffraction results in Fig. 1 and Table 3, the optimized chemically treated substrate A shows a crystallinity degree of 94.4% and contains, besides aluminium, crystalline phases of orthorhombic Al_2O_3 (PDF 00-052-0803, 45.76%) and hydrated aluminium oxides (54.24%): gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, PDF 00-002-0192) and gibbsite syn, $\text{Al}(\text{OH})_3$ (PDF 00-023-0018), with monoclinic structure. As expected, the presence of aluminium-oxygen based compounds on the chemically treated Al substrate is confirmed by EDS analysis: 96% Al and 4% O (weight percents). The surface morphology of this optimized substrate A, investigated using Scanning Electron Microscope, shows a porous structure as presented in Fig. 2a.

3.2. The alumina matrix optimization

For a better infiltration of the colored pigment in the substrate's pores, an additional layer of Al_2O_3 was deposited on the optimized substrate A by: a) immersion of Al substrate in a diluted sol of alumina for 24, 48 or 72 hours, and b) robotic spraying of diluted alumina sol, at $T = 130^\circ\text{C}$, using 5, 10 or 15 spraying sequences.

The influence of the immersion time and number of spraying sequences on the optical properties (thermal emittance, ε) of the alumina matrix was investigated and the results are presented in Table 2.

Tab. 2: The thermal emittance of alumina matrices obtained by depositing the Al_2O_3 layer on the Al substrate by immersion in the diluted sol, respectively by spraying the diluted sol at average temperature

Sample	A/AOSG24	A/AOSG48	A/AOSG72	A/AOSGs5	A/AOSGs10	A/AOSGs15
ε	0.06 ...0.19	0.08...0.17	0.14...0.20	0.24...0.35	0.37...0.40	0.38...0.43

It was observed that the values of the thermal emittance decrease ($\varepsilon < 0.2$) for the samples obtained by immersion in the diluted sol and significantly increase ($\varepsilon > 0.24$) for the sprayed alumina matrices. Therefore, from each series of alumina matrices there was selected, for further characterization, the sample with the lowest thermal emittance value: A/AOSG24, respectively A/AOSG24s5.

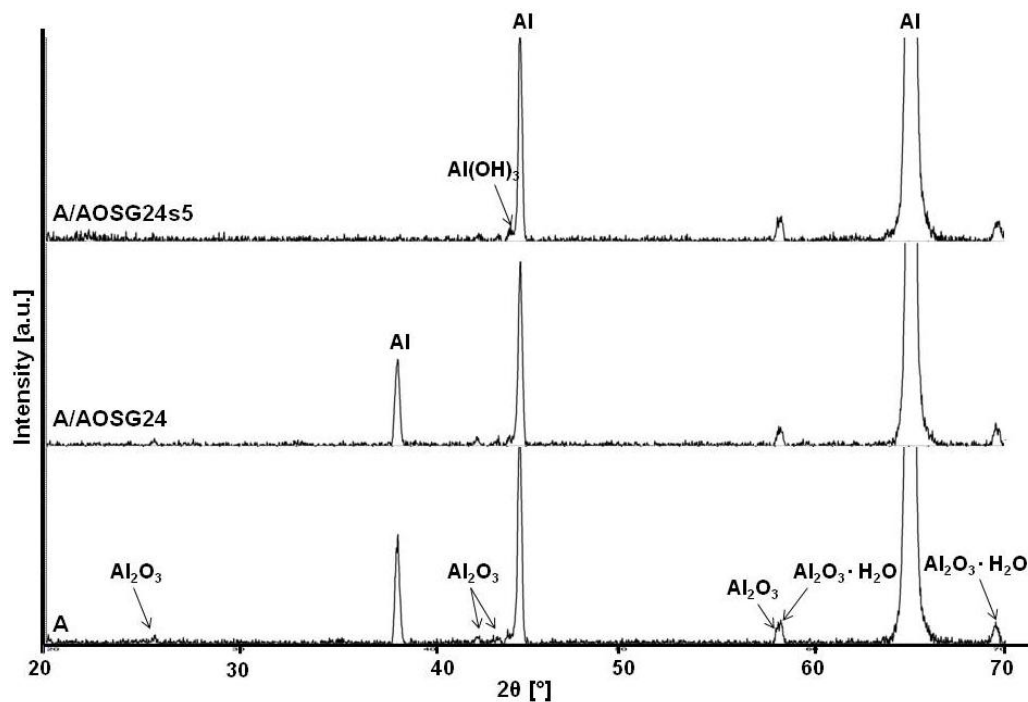


Fig. 1: XRD patterns of substrate A and alumina matrices

The X-Ray diffraction spectra, Fig. 1, show that both alumina matrices have polycrystalline structures, with crystalline phases similar to the A substrate, but with quite different compositions (weight %). The results in Table 3 show that using two different techniques for the alumina layer deposition on the Al substrate, causes no

significant changes in the crystallinity degree (92 - 94%), but significant changes in the crystalline phase compositions can be observed. In the matrix obtained by spraying the diluted sol on the Al substrate, the anhydrous Al_2O_3 content significantly decreases, compared to that of Al substrate, respectively Al matrix A/AOSG24. It is expected that a lower content of alumina in the matrix leads to less suitable optical properties (higher ϵ), reducing the optical performance of the matrix A/AOSG24s5.

Moreover, the line attributed to the Al crystalline phase ($2\theta = 38.54^\circ$) is not detected in XRD pattern of sample A/AOSG24s5, which means that the layer deposited by spraying is thicker than that deposited by immersion. In this case, increasing the thickness of the matrix layer may influence the matrix morphology by covering the pores of the substrate, resulting in denser layers that have a reduced possibility of pigment film/particles infiltration.

Tab. 3: The crystallinity and estimative crystalline phases composition of the optimized Al substrate and alumina matrices

Sample	Crystallinity [%]	Al_2O_3 [%]	Gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ [%]	Gibbsite syn, $\text{Al}(\text{OH})_3$ [%]
A	94.4	45.76	52.12	2.12
A/AOSG24	93.9	59.98	32.53	7.49
A/AOSG24s5	92.1	26.35	67.30	6.35

The elemental composition analyzed by EDS, represented in Fig. 2, gives information about the surface composition and, consequently, about the growth and adhesion among the successive layers, allowing the most accurate design of the alumina and the final absorber layers. It is interesting to note that in the matrix obtained by immersion of the Al substrate in diluted sol (A/AOSG24), the increase in the oxygen content is not observed, as expected. Instead, the aluminium content in matrices significantly decreases, especially in the A/AOSG24s5 sample, where the Al content is three times lower than in the substrate, that can be the result of the thicker and more denser layer. However, for the investigated alumina matrices, the EDS results mostly confirm the differences highlighted in XRD composition. The presence of amorphous carbon/carbon compounds in the alumina matrices is due to the PEG additive used in alumina sol synthesis to control the hydrophilic/hydrophobic balance and support the gelation and phase separation processes (Milea et. al, 2013).

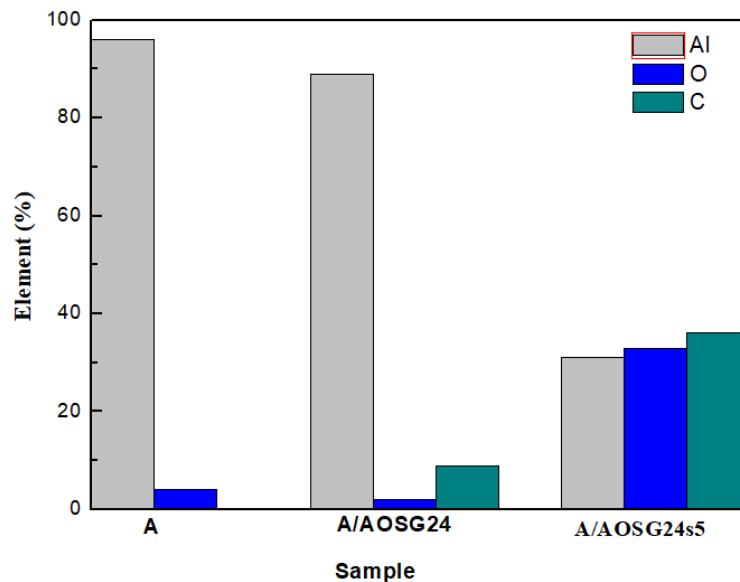


Fig. 2: Elemental composition graphs for Al substrate and alumina matrices

The surface morphology, along with the composition and crystalline structure, is considered an important property with consequences on the optical performances of an absorber material. One of the most efficient and affordable solution to improve the heat transfer and energy efficiency in a solar coating is to use porous materials as components (Rashidi et al., 2017). Both the chemically pre-treated substrate A and the matrix A/AOSG24 show relative porous morphologies with slightly larger pores for the matrix, as is shown in Fig. 3b.

The highly porous Al substrate or/and the alumina matrix are expected to represent good hosts for further infiltration with pigment layers to develop efficient solar selective absorber coatings, for coloured solar thermal collectors.

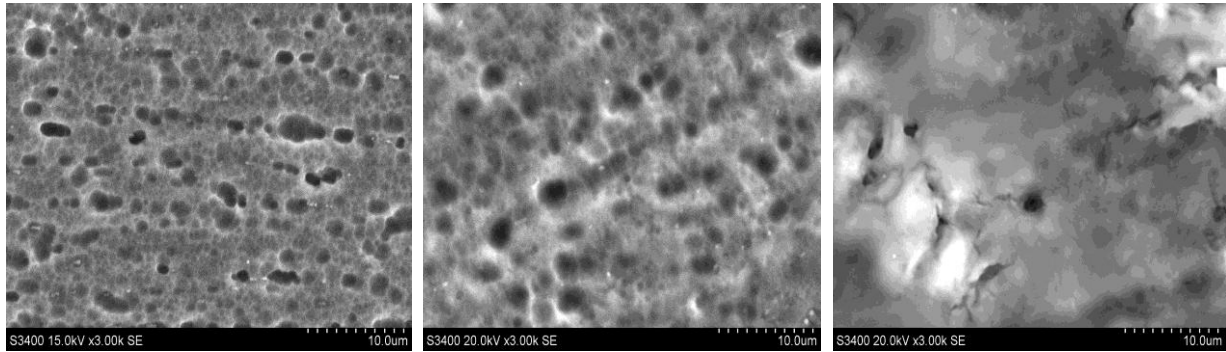


Fig. 3: a) SEM image of optimized substrate A

Fig. 3: b) SEM image of alumina matrix A/AOSG24

Fig. 3: c) SEM image of alumina matrix A/AOSG24s5

According to the SEM image in Fig. 3c, the morphology of the alumina layer deposited on the optimized Al substrate by spraying, is quite different (with micro-cracks), comparing with morphologies of Al substrate (Fig. 3a) and alumina layer obtained by immersion (Fig. 3b). Moreover, the alumina layer is thicker and covers a large part of the substrate pores, confirming the EDS results. Consequently, the light reflections on this surface are significantly reduced, confirming the increase (almost double) of the thermal emittance value, thus decreasing the optical performances of the alumina matrix A/AOSG24s5.

The solar absorptances (α), calculated from the reflectance spectra of the samples and presented in Table 4, slightly increases for the alumina matrix, while the thermal emittances have different variation: significantly decreases, for matrix obtained by immersion, and are close to that of the substrate, for the matrix obtained by spraying.

Tab. 4: Optical properties for optimized Al substrate and alumina matrices

Sample	α	ϵ	S
A	0.13	0.22	0.59
A/AOSG24	0.16	0.06	2.66
A/AOSG24s5	0.19	0.24	0.79

These results are expected, considering the matrices chemical compositions and surface morphologies and are in good agreement with those obtained from the crystalline phases composition and elemental analysis.

4. Conclusions

The first step in designing colored solar selective absorber coatings is the obtaining of an alumina matrix layer with controlled morphology, to be further infiltrated with metal particles or/and inorganic pigment(s).

The paper reports on the development, characterization and optimization (using spectral selectivity S as output property), of the alumina matrix (Al/Al_2O_3) obtained by the deposition of the alumina layer on the optimized, chemically pre-treated aluminum substrate, using two simple and low-cost techniques: immersion and robotic spraying of a diluted alumina sol.

According to the crystalline phases composition and surface morphology, the alumina matrix obtained by immersing the Al substrate in a diluted alumina sol for 24 hours shows the best optical results: $\alpha = 0.16$, $\epsilon = 0.06$ and $S = 2.66$. This matrix is suitable for further infiltration of yellow (based on V_2O_5) and green (based on CuS) pigment particles to develop colored absorber coatings, for market-acceptable solar thermal collectors with increased architectural acceptance, for facades integration in Nearly Zero Energy Buildings.

5. References

Alami, A.H., Aokal, K., 2018. Enhancement of spectral absorption of solar thermal collectors by bulk graphene addition via high-pressure graphite blasting. *Energ. Convers. Manage.* 156, 757-764. <https://doi.org/10.1016/j.enconman.2017.11.040>

Balakrishnan, G., Tripura Sundari, S., Ramaseshan, R., Thirumurugesan, R., Mohandas, E., Sastikumar, D., Kuppasami, P., Kim, T.G., Song, J.I., 2013. Effect of substrate temperature on microstructure and optical properties of nanocrystalline alumina thin films. *Ceram. Int.* 39, 9017-9023. <https://doi.org/10.1016/j.ceramint.2015.08.145>

Bermel, P., Lee, J., Joannopoulos, J.D., Celanovic, I., Soljačić, M., 2012. Selective solar absorbers - Chapter 7. in: *Annual Review of Heat Transfer 15*, Begell House Inc., pp. 231-254.

Birkholz, M., 2005. Thin film analysis by X-Ray Scattering. Wiley-VCH Verlag GmbH & Co.

Céspedes, E., Wirz, M., Sánchez-García, J.A., Alvarez-Fraga L., Escobar-Galindo, R., Prieto, C., 2014. Novel Mo-Si₃N₄ based selective coating for high temperature concentrating solar power applications. *Sol. Energy Mater. Sol. Cells* 122, 217-225. <https://doi.org/10.1016/j.solmat.2017.08.021>

Duta A., Isac L., Milea A., Ienei E., Perniu, D., 2014. Coloured Solar-thermal Absorbers – A Comparative Analysis of Cermet Structures. *Energy Procedia* 48, 543-553. <https://doi.org/10.1016/j.egypro.2014.02.064>

Estrella-Gutiérrez, M.A., Lizama-Tzec, F.I., Arés-Muzio, O., Oskam, G., 2016. Influence of a metallic nickel interlayer on the performance of solar absorber coatings based on black nickel electrodeposited onto copper. *Electrochim. Acta* 213, 460-468. <https://doi.org/10.1016/j.electacta.2016.07.125>

Fernandes, J.C.S., Nunes, A., Carvalho, M.J., Diamantino, T.C., 2017. Degradation of selective solar absorber surfaces in solar thermal collectors - An EIS study. *Sol. Energy Mater. Sol. Cells* 160, 149-163. <http://dx.doi.org/10.1016/j.solmat.2016.10.015>

Isac, L., Nicoara, L., Panait, R., Enesca, A., Perniu, D., Duta, A., 2017. Alumina matrix with controlled morphology for colored spectrally selective coatings. *Environ. Eng. Manag. J.* 16(3), 715-724.

Isac, L., Panait, R., Enesca, A., Bogatu, C., Perniu, D., Duta, A., 2018. Development of black and red absorber coatings for solar thermal collectors, in: Visa, I., Duta, A. (Eds.), *Nearly Zero Energy Communities*. Springer Proceedings in Energy. Springer International Publishing AG, pp. 263-282. https://doi.org/10.1007/978-3-319-63215-5_20

Khatibani, A.B. and Rozati, S.M., 2015. Optical and morphological investigation of aluminium and nickel oxide composite films deposited by spray pyrolysis method as a basis of solar thermal absorber. *Bull. Mater. Sci.* 38 (2), 319-326. <https://doi.org/10.1007/s12034-015-0880-5>

Milea C.A., Ienei E., Bogatu C., Duta A., 2013. Sol-gel Al₂O₃ powders—matrix in solar thermal absorbers. *J.Sol-Gel Sci. Techn.* 67, 112-120. <https://doi.org/10.1007/s10971-013-3056-z>

Purghel, E., Voinea, M., Isac, L., Duta, A., 2008. Optical properties of Ni/NiO_x as infiltration agent in cermet solar Ir absorber. *Rev. Chim-Bucharest* 59, 469-471.

Rashidi, S., Esfahani, J.A., Rashidi, A., 2017. A review on the applications of porous materials in solar energy systems. *Renew. Sust. Energ. Rev.* 73, 1198-1210. <https://doi.org/10.1016/j.rser.2017.02.028>

Sun, X-Y., Sun, X-D., Li, X-G., Wang Z-Q., He, J., Wang B-S., 2014. Performance and building integration of all-ceramic solar collectors. *Energ. Buildings*, 75, 176-180. <https://doi.org/10.1016/j.enbuild.2014.01.045>

Visa, I., Moldovan, M.D., Comsit, M., Neagoe, M., Duta, A., 2017. Facades integrated solar-thermal collectors - challenges and solutions, *Energy Procedia*, 112, 176-185. <https://doi.org/10.1016/j.egypro.2017.03.1080>

Acknowledgements

We hereby acknowledge the structural funds project PRO-DD (POS-CCE, O.2.2.1., ID 123, SMIS 2637, No 11/2009) for providing the infrastructure used in this work and the project PNIII-PED SOL_TRI_COL, contract no. 58/2017 financed by UEFISCDI.