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Optical properties and structure of Al2O3/CoCuMnOx bilayer for solar selective absorbers.

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Abstract

Solar absorbers are the backbone of solar harvesting systems for various applications, especially concentrating solar power systems. The absorber surface must have higher absorbtivity and lower emissivity of solar radiation which is achieved by applying selective coating on the absorber surface. In this work a bilayer coating is prepared and evaluated. It consists of two layers; a metal oxide layer i.e Al2O3, and CoCuMnOx spinel film. The plasma thermal spray process was used for applying the Al_2O_3 *layer, and the sol-gel dip coating technique was used for the CoCuMnOx layer. Optical properties of the coatings, namely absorptivity (α) and emissivity (ε) were measured for the* Al_2O_3 *layer and after sol-gel coating was applied, the selectivity (α-0.5*ε) was then calculated. The achieved selectivity of the* Al_2O_3 *layer was 0.624 and after applying the sol-gel dip coating, it raised to 0.764. The deposited coatings were analyzed using Optical microscopy, SEM, EDX, and XRD.*

Keywords: *Solar energy, Selective solar absorber, bilayer coating, aluminum oxide, CoCuMnOx*

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I. INTRODUCTION

The need to reduce the use of conventional energy sources and achieve sustainability, solar energy, which is clean, cheap, and free of toxic emissions[1]and has more potential than all other renewable energy sources, is becoming increasingly important. Even so, there is enough solar energy to meet the entire world's energy needs[2]. The demand to switch to renewable energy sources like solar energy, which is abundant, free, and has commercial potential, has grown significantly during the past decade. Several uses, including solar heating, solar thermo-photovoltaics, and solar thermo-electricity, can benefit from effectively capturing solar heat. However, compared to the potential of the sun, very little solar energy is being converted into useful energy[3].

A significant challenge is the energy efficiency of manufacturing processes for solar energy system components. The optically selective coating on the solar absorber, which acts as an infrared mirror and should, in theory, behave as a black body, absorbing the greatest amount of the incoming solar radiation, is one of the fundamental components of a solar thermal collector. The invention of a solar selective coat that can be stable and resilient at high temperatures has had a significant impact on improving the efficiency of solar absorbers of all types[4]. High UV absorptivity and low thermal emissivity in the near-infrared (NIR) and far infrared (FIR) wavelength bands are required for the selective coat. These can be attained by a substance that reflects less than 10% of UV light and more than 90% of IR light. The absorptivity/emissivity ratio (α/ε), which combines absorptivity and emissivity, can be used to describe a material's selectivity factor; the higher the selectivity ratio, the more promising the material will be for certain solar applications[5]. To achieve the aforementioned fundamental properties of a spectrally selective solar absorber surface, various configurations based on various physical principles, such as optical trapping, selective coatings, composite films, absorbing semiconductor-metal tandems, multilayer thin films, or combinations of them, can be developed[6].

For absorber coating designed to operate at high temperatures, the required attributes to possess are excellent solar selectivity, high-temperature stability, high structural and chemical stability, ability to resist oxidation, corrosion, humidity, hardness, and scratch[7]. Due to its superior hardness, chemical stability, and refractory character[8][9], it is noticeable that Al2O3 received a great deal of attention in many studies of a selective coating for solar absorbers. It is used either as a host matrix for a dielectric absorber known as cermets such as cermet MoSi2–Al2O3[10], Pt– Al2O3[6], and/or an anti-reflection layer for a multilayer absorber such as TiAlNx/TiAlNy/Al2O3 tandem[11], and Al2O3-WC nanocomposite ceramic[12].

Sol-gel thin films are employed in a variety of applications today, including sensor devices, electronics, and energy conversion. The simplicity with which coatings are created by simply dipping the substrate into an appropriate colloidal solution and withdrawing in a controlled manner, eliminating more expensive deposition procedures, is the fundamental benefit of the sol-gel film deposition process. The ability to create thin films with a consistent chemical composition is another advantage of the sol-gel method[5], [13].In the study of selective coatings utilizing sol-gel techniques, ternary spinel-like oxides such as CoCuMnOx is among the most interesting[14],[5]. Joly et al [4] studied the effect of a single layer of Cu-Co-Mn-O on stainless steel, a solar absorptance of 0.86 ± 0.01 was reached for a thermal emissivity of 0.11 ± 0.01. Eletriby et al [5] studied the effect of different concentrations of CoCuMnOx sol-gel and the different withdrawal rates on the optical properties of the coat, the best conditions were at molar ratio/60 where the absorbtivity reached 0.91 and emissivity of 0.09. in [13] investigated the effect of substrate material by applying CoCuMnOx on copper and aluminum substrates, the copper substrate achieved 0.90 absorptivity and 0.011 emissivity.

Stainless steel is a good candidate for substrate material. It can be used for receiver tubes for applications utilizing concentrated solar power (CSP), such as solar thermal electricity generation facilities, as well as cushion absorbers for domestic hot water generation. due to its weldability and mechanical stability at high temperatures and has distinctive characteristics represented in forming and welding properties[5], and yet has a relatively high emissivity as a base metal than other metals like aluminum and copper[4][5][13]. Taha et al [15] studied the selectivity of roughened stainless steel (Ra=1.35μ) is very low (α=0.824 and ε=0.532 without annealing and α=0.902 and ε=0.309 if annealed at 450 °C.

This work is an attempt to achieve a good solar selective coat through a bilayer structure where the interference effect improves the absorption[8]. A layer of Al2O3 was added to the stainless steel substrate by thermal plasma spray, then the coated substrates were dipped in a CoCuMnOx sol-gel and the optical properties are studied.

II. Methodology

1.1.1 Fractionation Section

Substrate material has to be specially prepared to maintain acceptable adhesion of the coating to the base metal. At first, stainless steel samples of 2 mm thickness were cut into strips of 3 × 10 cm. Then, the different surface roughness of the samples was conducted by sandblasting to ensure enhanced mechanical adhesion between the coating and the substrate. Surface roughness was measured by TAYLOR-HOBSON Surtronic 3 surface roughness tester. The last step involved degreasing using ultrasonic cleaning of the samples by immersing them into acetone and sonicating them in ISOLAB ultrasonic bath for 10 min at room temperature to ensure the removal of any grease or sand residue. Samples were then dried with hot air and kept ready for the coating process.

The procedure of preparation of sol-gel coating of CoCuMnOx was previously discussed and shown in detail in several previous research [5][13]. The main precursor of the solution is based on three main metal oxides: Co II acetate, Cu II nitrate, and Mn II acetate. The solvents used were ethylene glycol and absolute ethanol at a molar ratio/60.

The Alumina layer was added to the substrate with different surface roughness using PLASMA-TECHNIK AG SWITZERLAND, the powder used for plasma thermal spray was METCO 101NS (Alumina 3% titania powders). Conventional atmospheric plasma spraying set up with F4-MB is utilized where the heat source (plasma) is initiated by the generation of a high-density arc current in the space between an anode and a cathode with hydrogen (diatomic gas) and argon (monatomic gas). The temperatures of these gases were elevated up to 15,000 °C and the flow was expanded to reach supersonic gas exit velocities. The primary plasma gas is Ar at a pressure of 0.13 MPa with a flow rate of 46 SLPM, the secondary gas is H2 at a pressure of 0.15 MPa with a flow rate of 8.1 SLPM, the powder feed rate is 50 gm/min, and the plasma jet current is 600 A.

The gel needed to be re-agitated at a proper speed at about 50 °C before dipping to maintain its viscosity-dense form before dipping. A tensile test machine was used to control the withdrawal rate of the substrate from the sol-gel at 1cm/min. The first layer was added to the substrate and left for 24 hours then the second layer was added. Intermediate heat treatment at 450°C for 30 minutes was applied to the coat.

III. Characterization and testing

For each sample, the optical characteristics, including emissivity and absorptivity, were assessed at three separate locations inside the coating. The average value for the three samples was determined. Thermo Finnigan's Nicolet 380 FT-IR spectrometer was used to assess emissivity (ε), while the by Spectrophotometer Shimadzu UV 3600 Uv-VIS-NIR was used to detect absorption (scan range: 0.2-0.9 μm). This equation was used to determine absorbtivity:[16][17][8]

$$\propto = \frac{\int_{\lambda 1}^{\lambda 2} (I_0(\lambda) * (1 - R(\lambda))d\lambda}{\int_{\lambda 1}^{\lambda 2} I_0(\lambda)\, d\lambda} \qquad (1)$$

where: R is the reflectance obtained in the entire scan wavelength range, Io (λ) is the spectral power density of the solar radiation air mass 1.5, λ1, and λ2 are the limits of the wavelength range.

To calculate emissivity the following equation is used:[16][17][8]

$$\varepsilon = \frac{\int_{\lambda 1}^{\lambda 2} (P(\lambda) * (1 - R(\lambda))d\lambda}{\int_{\lambda 1}^{\lambda 2} P(\lambda)d\lambda} \qquad (2)$$

where: R is the reflectance obtained experimentally from FTIR in the entire scan wavelength range. P(λ) is the spectral radiance of a black body at a temperature of 100 °Ccoherent with the medium temperature applications. λ1 and λ2 are the limits of the wavelength range.

Selectivity factor can be defined by the formula $(\alpha_{sol} - 0.5 \times \varepsilon_{therm})$[18]; the higher the selectivity ratio the more promising the material will be for such solar applications[5].

Using the FESEM QUANTA FEG 250 Made in the Netherlands and the EdX EDAX Genesis Made in the USA instrument, SEM/EDX examination was used to examine the surface topography of a few different samples.

IV. RESULT AND DISCUSSION

The stainless steel was used as a base metal to study the effect of multi-layer selective coating, the first layer of alumina was deposited on the substrate surface by plasma thermal spray then the second layer of CoCuMnOx was added on the first layer via sol-gel dipping. Figure 1 shows the coated samples before and after heat treatment, the surrounding area is the area chosen for performing characterization.

(a) (b)

Figure 1: samples with sol-gel layer (a) after 24 hours from the first dip, and (b) after a second dip and heat treatment.

The substrates were prepared at different surface roughness Ra. The resulting surface roughness was measured using TAYLOR-HOBSON Surtronic 3 surface roughness tester before and after the thermal plasma spray. It is noticed that the alumina layer has high constant roughness at about 5.7 µm despite the value of substrate roughness, this is due to the process mechanism where plasma-sprayed coatings are created by gradually solidifying drops of liquid or partially melted material onto the target substrate which produces porous surface[9]. The benefit of the rough surface is that it enhances the adhesion of the sol-gel layer[5], but the sol-gel layer will act as a sealing which in turn reduces the pores which affect the light trapping[19]. So, the optical properties would be significantly affected. Figure 2 shows the difference in reflectivity in the U-V range between a stainless steel substrate coated with alumina (METCO 101NS) with and without a CoCuMnOx coat. it is noticed that the sol-gel layer decreased the reflectivity in the UV range, this means the absorptivity increased due to the decrease in reflectivity as illustrated in Figure 2, and the absorbtance calculated by equation (1) increased from (α=0.794 to 0.884).

The infrared reflection was measured on the alumina layer before dipping in sol-gel, then measured again after adding the CoCuMnOx layer by a sol-gel dip coating process. Figure 3 shows the effect of the sol-gel layer on the reflectance in the infrared range (2500-25000 nm). The emissivity calculated using equation (2) decreased from 0.34 to 0.24. Figure 4 summarizes the effect of sol-gel on the absorbtivity, emissivity, and consequently, selectivity of samples, the selectivity of the samples increased from 0.624 to 0.764

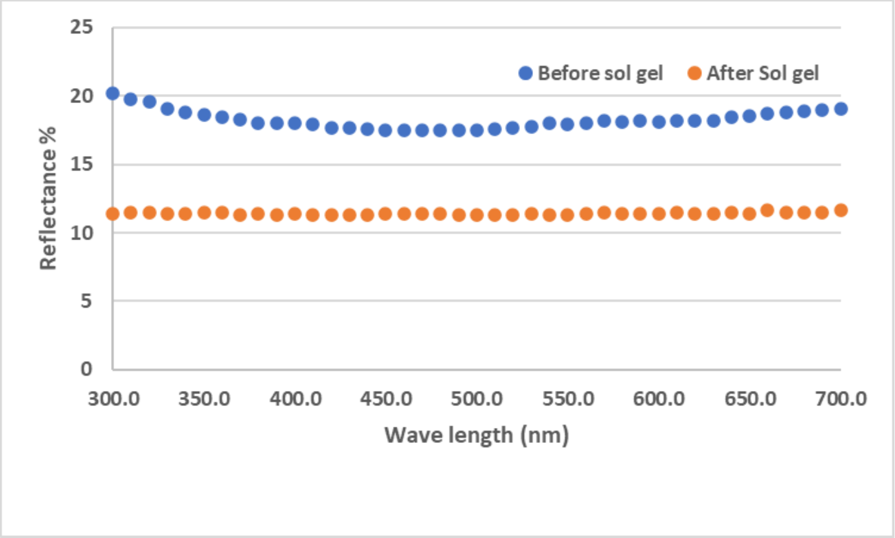


Figure 2: Reflectance measurements in UV range for measuring absorptivity of stainless steel samples coated with Al2O3 and after the sol-gel coating is applied.

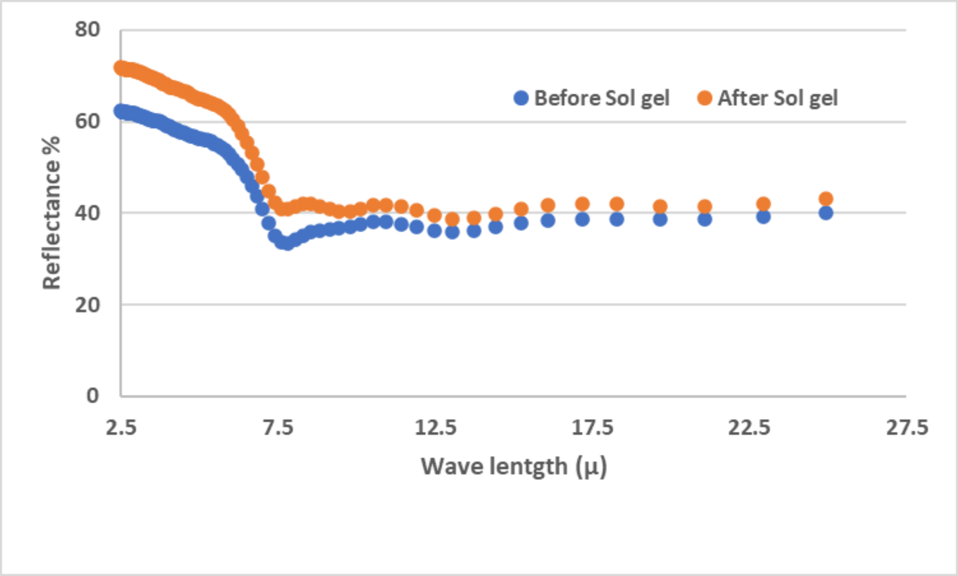


Figure 3: Reflectance measurements in the IR range for measuring the emissivity of samples before and after the dipping-heat treatment cycle.

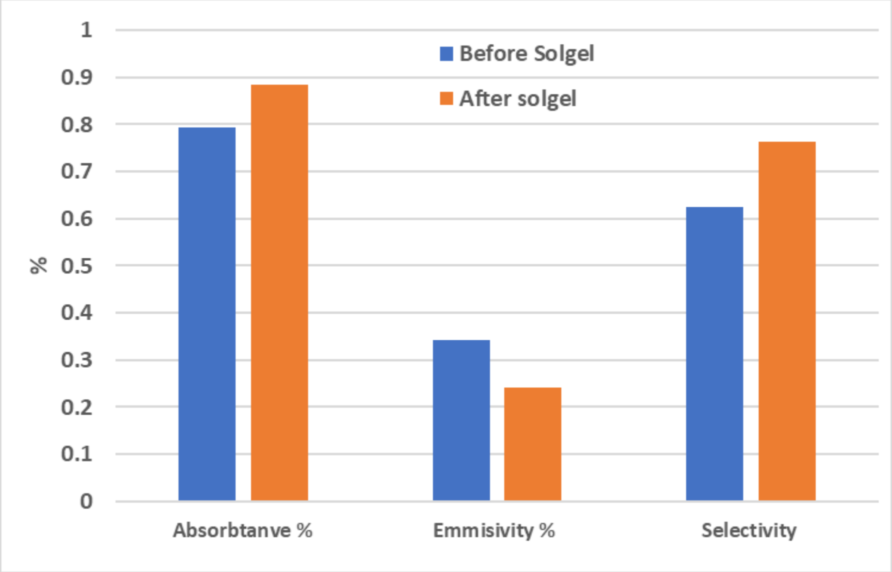


Figure 4: Effect of sol-gel layer on the absorbtivity, emissivity, and consequently the selectivity

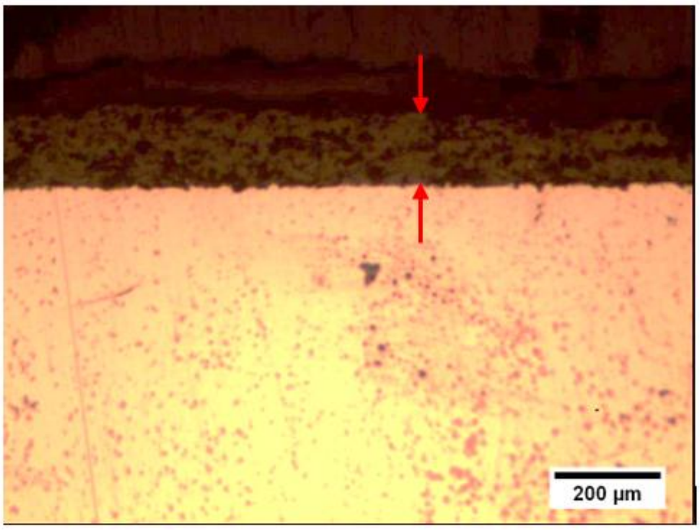


Figure 5: : Coating layer image depicted by optical microscopy indicating the thickness of the coat.

The coating thickness for chosen samples was measured using FEROX PL optical microscopy. Ten readings were taken along the sample, and the average thickness of the coat was 141.579±10.36 µm for both layers of alumina and CoCuMnOx, Figure 5 shows an image of the coating by the optical microscope

Figure 6 shows the SEM image of the sol-gel coated sample. It is shown from the image that the surface topography consists of grooves and pores; this act as a textured surface that acts as a trap of light [5]. Figure 7 illustrates the EDX analysis which shows the elements of the coating (O, Al, Si, Ti, Co, Cu, and Mn) and the substrate elements (Fe, Ni, and Cr).

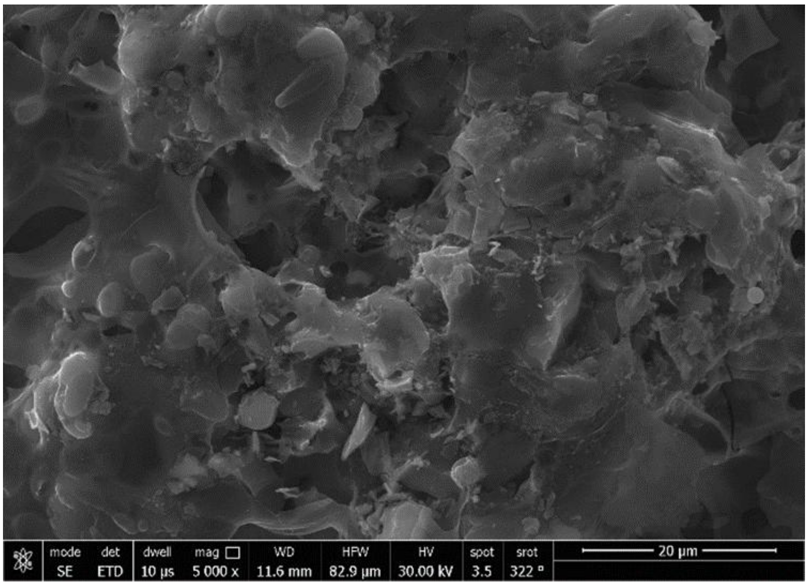
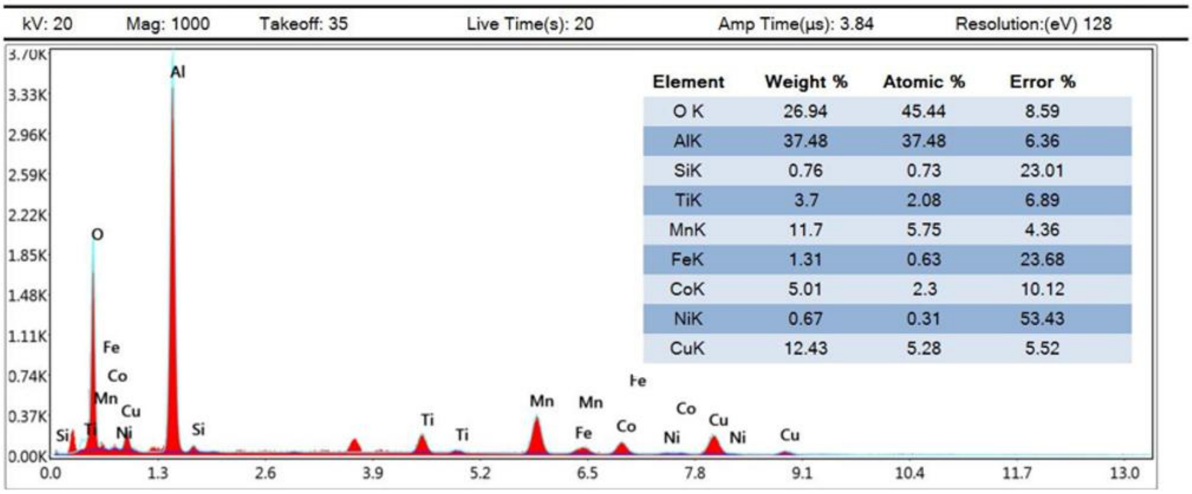


Figure 6: SEM image of the optimum sample after the dip-heat cycle. Magnification X 5000



Element	Weight %	Atomic %	Error %
O K	26.94	45.44	8.59
AlK	37.48	37.48	6.36
SiK	0.76	0.73	23.01
TiK	3.7	2.08	6.89
MnK	11.7	5.75	4.36
FeK	1.31	0.63	23.68
CoK	5.01	2.3	10.12
NiK	0.67	0.31	53.43
CuK	12.43	5.28	5.52

Figure 7:EDX analysis of the optimum sample after the dip-heat cycle.

In an attempt to investigate the compounds formed in coated samples, XRD analysis was applied to the optimum sample that attained the best optical properties. Figure 8 illustrates that the coat contains spinel oxides such as copper oxide, manganese oxide, copper manganese oxide, and the spinel (CoCuMnOx) in addition to the alumina from the first layer.

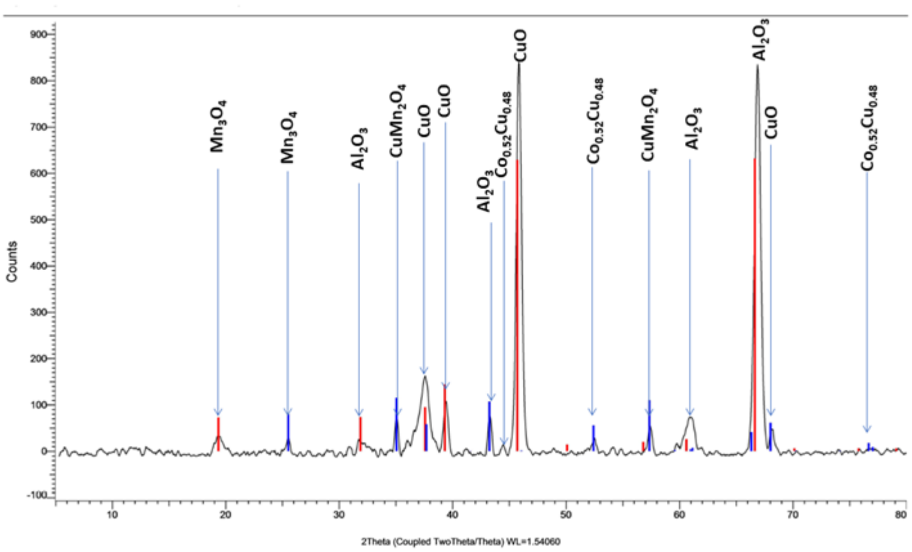


Figure 8:XRD analysis of the coated sample after sol-gel dip coating.

V. CONCLUSION

In this research, a bilayer coating was prepared and tested for optical properties. It is composed of Al2O3 coating applied on stainless steel substrate using plasma thermal spray and a CoCuMnOx spinel film applied on the Al2O3 layer. The Al2O3 layer achieved an absorbtivity of 0.794 and an emissivity of 0.34. The absorbtivity increased to 0.884 and the emissivity decreased to 0.24 by applying the CoCuMnOx sol-gel coat, which increased the selectivity of samples from 0.624 to 0.764. The results reveal that the bilayer coating can give relatively good optical properties for use as absorbers of solar radiation. This improvement is explained by the surface topography of the samples which consists of grooves and pores which act as a trap of light making incident light reflect again and again in these pores until most of it is absorbed.

REFERENCES

[1] M. J. Kadhim, K. A. Sukkar, and A. S. Abbas, "Copper Thin Film Deposited by PVD on Aluminum AA4015 Substrate for Thermal Solar Application," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 518, no. 3, 2019, doi: 10.1088/1757-899X/518/3/032048.

[2] A. A. M. Murugan , A. Saravanan , P.V. Elumalai , Pramod Kumar , C. Ahamed Saleel , Olusegun David Samuel, Muji Setiyo , Christopher C. Enweremadu, "An overview on energy and exergy analysis of solar thermal collectors with passive performance enhancers," *Alexandria Eng. J.*, vol. 61, no. 10, pp. 8123–8147, Oct. 2022, doi: 10.1016/j.aej.2022.01.052.

[3] N. El-Mahallawy, M. R. A. Atia, A. Khaled, and M. Shoeib, "Design and simulation of different multilayer solar selective coatings for solar thermal applications," *Mater. Res. Express*, vol. 5, no. 4, p. 46402, 2018, doi: 10.1088/2053-1591/aab871.

[4] A. M. Joly, Antonetti, Y, Python, M, Gonzalez, M, Gascou, T, Hessler, A, Schueler, "Energy-efficient sol-gel process for production of novel nanocomposite absorber coatings for tubular thermal collectors," *Cisbat 2013*, pp. 11–16, 2013.

[5] N. E. M. ; M. S. ; S. Eletriby, "Effect of Sol-Gel Process Parameters on Optical Properties of CuCoMnOx Selective Coat for Solar Energy Applications," vol. 12, no. 4, pp. 41–48, 2016, doi: 10.7537/marsjas12041605.Keywords.

[6] Z. Y. Nuru, D. E. Motaung, K. Kaviyarasu, and M. Maaza, "Optimization and preparation of Pt-Al2O3 double cermet as selective solar absorber coatings," *J. Alloys Compd.*, vol. 664, 2016, doi: 10.1016/j.jallcom.2015.12.201.

[7] O. M. Bo Liu , ChunyuWang , Shahab Bazri , Irfan Anjum Badruddin , Yasin Orooji , Samrand Saeidi, Somchai Wongwises, "Optical properties and thermal stability evaluation of solar absorbers enhanced by nanostructured selective coating films," *Powder Technol.*, vol. 377, pp. 939–957, 2021, doi: 10.1016/j.powtec.2020.09.040.

[8] E. A. L. Rebouta , A. Sousa , P. Capela , M. Andritschky , P. Santilli , A. Matilainen , K. Pischowb, N.P. Barradas, "Solar selective absorbers based on Al2O3:W cermets and AlSiN/AlSiON layers," *Sol. Energy Mater. Sol. Cells*, vol. 137, pp. 93–100, 2015, doi: 10.1016/j.solmat.2015.01.029.

[9] M. L. Benea and L. P. Benea, "The improvement of steel properties using Al2O3 coatings deposited by plasma spraying," *J. Phys. Conf. Ser.*, vol. 1426, no. 1, p. 12010, 2020, doi: 10.1088/1742-6596/1426/1/012010.

[10] Y. Xue, C. Wang, Y. Sun, W. Wang, Y. Wu, and Y. Ning, "Preparation and spectral properties of solar selective absorbing MoSi 2-Al2O3 coating," *Phys. Status Solidi Appl. Mater. Sci.*, vol. 211, no. 7, pp. 1519–1524, 2014, doi: 10.1002/pssa.201330658.

[11] A. Soum-Glaude, A. Le Gal, M. Bichotte, C. Escape, and L. Dubost, "Optical characterization of TiAlNx/TiAlNy/Al2O3 tandem solar selective absorber coatings," *Sol. Energy Mater. Sol. Cells*, vol. 170, no. February, pp. 254–262, 2017, doi: 10.1016/j.solmat.2017.06.007.

[12] X. H. Gao, C. B. Wang, Z. M. Guo, Q. F. Geng, W. Theiss, and G. Liu, "Structure, optical properties and thermal stability of Al2O3-WC nanocomposite ceramic spectrally selective solar absorbers," *Opt. Mater. (Amst).*, vol. 58, pp. 219–225, 2016, doi: 10.1016/j.optmat.2016.05.037.

[13] N. El Mahallawy, M. Shoeib, and Y. Ali, "Application of CuCoMnO x coat by sol gel technique on aluminum and copper substrates for solar absorber application," *J. Coatings Technol. Res.*, vol. 11, no. 6, pp. 979–991, Nov. 2014, doi: 10.1007/s11998-014-9592-9.

[14] F. Taha, N. El Mahallawy, and M. Shoeib, "A study of sol gel process parameters on CoCuMnO x selective coating characteristics," *Mater. Res. Express*, vol. 7, no. 2, p. 026410, Feb. 2020, doi: 10.1088/2053-1591/ab70de.

[15] F. Taha, N. El Mahallawy, and M. Shoeib, “Effect of different carbon allotropes on optical properties of CoCuMnOx solar selective coating,” *Eng. Sci. Technol. an Int. J.*, vol. 33, p. 101086, 2022, doi: 10.1016/j.jestch.2021.101086.

[16] R. Kumar, B. Usmani, and A. Dixit, “W/SS thin film as high temperature infrared reflector for solar thermal applications: intrinsic properties and impact of residual oxygen,” *Mater. Res. Express*, vol. 6, no. 10, p. 106408, Aug. 2019, doi: 10.1088/2053-1591/ab3757.

[17] A. Khaled, N. El-Mahallawy, M. Shoeib, and M. R. A. Atia, “PH value variation for effective solar energy harnessing of copper oxide based sol-gel prepared coatings,” *Surf. Topogr. Metrol. Prop.*, vol. 7, no. 2, 2019, doi: 10.1088/2051-672X/ab161b.

[18] Z. Chen, A. Jain, and T. Boström, “Simulation of Anti-reflection Coated Carbonaceous Spectrally Selective Absorbers,” *Energy Procedia*, vol. 58, no. 1876, pp. 179–184, 2014, doi: 10.1016/j.egypro.2014.10.426.

[19] M. Z. Pakhuruddin, J. Huang, J. Dore, and S. Varlamov, “Rear texturing for light-trapping in laser-crystallised silicon thin-film solar cells on glass,” *Sol. Energy*, vol. 166, no. January, pp. 213–219, May 2018, doi: 10.1016/j.solener.2018.03.055.