Cost Efficient Receiver Tube Technology for Eco-Friendly Concentrated Solar Thermal Applications

M. Shiva Prasad, S. R. Atchuta, T. Vijayaraghavan, S. Sakthivel

Abstract—The world is in need of efficient energy conversion technologies which are affordable, accessible, and sustainable with eco-friendly nature. Solar energy is one of the cornerstones for the world's economic growth because of its abundance with zero carbon pollution. Among the various solar energy conversion technologies, solar thermal technology has attracted a substantial renewed interest due to its diversity and compatibility in various applications. Solar thermal systems employ concentrators, tracking systems and heat engines for electricity generation which lead to high cost and complexity in comparison with photovoltaics; however, it is compatible with distinct thermal energy storage capability and dispatchable electricity which creates a tremendous attraction. Apart from that, employing cost-effective solar selective receiver tube in a concentrating solar thermal (CST) system improves the energy conversion efficiency and directly reduces the cost of technology. In addition, the development of solar receiver tubes by low cost methods which can offer high optical properties and corrosion resistance in an open-air atmosphere would be beneficial for low and medium temperature applications. In this regard, our work opens up an approach which has the potential to achieve cost-effective energy conversion. We have developed a highly selective tandem absorber coating through a facile wet chemical route by a combination of chemical oxidation, sol-gel, and nanoparticle coating methods. The developed tandem absorber coating has gradient refractive index nature on stainless steel (SS 304) and exhibited high optical properties ($\alpha \leq 0.95$ & $\varepsilon \leq 0.14$). The first absorber layer (Cr-Mn-Fe oxides) developed by controlled oxidation of SS 304 in a chemical bath reactor. A second composite layer of ZrO_2-SiO_2 has been applied on the chemically oxidized substrate by So-gel dip coating method to serve as optical enhancing and corrosion resistant layer. Finally, an antireflective layer (MgF_2) has been deposited on the second layer, to achieve > 95% of absorption. The developed tandem layer exhibited good thermal stability up to 250 °C in open air atmospheric condition and superior corrosion resistance (withstands for > 200h in salt spray test (ASTM B117)). After the successful development of a coating with targeted properties at a laboratory scale, a prototype of the 1 m tube has been demonstrated with excellent uniformity and reproducibility. Moreover, it has been validated under standard laboratory test condition as well as in field condition with a comparison of the commercial receiver tube. The presented strategy can be widely adapted to develop highly selective coatings for a variety of CST applications ranging from hot water, solar desalination, and industrial process heat and power generation. The high-performance, cost-effective medium temperature receiver tube technology has attracted many industries, and recently the technology has been transferred to Indian industry.

M.Shiva Prasad is with the International Advanced Research Centre for Powder Metallurgy and new Materials (ARCI), Hyderabad, 500005, India (phone: +91-9490409646; e-mail: prasadshiva364@gmail.com).

S.R. Atchuta is with the ARCI, Hyderabad, 500005, India (phone: +91-9493848884; e-mail: atchuta@project.arci.res.in).

T. Vijayaraghavan is with the ARCI, Hyderabad, 500005, India (phone: +91-8754000460; e-mail: ragavan07@gmail.com).

S. Sakthivel is with the ARCI, Hyderabad, 500005, India (corresponding author; phone: +91-9490760104; e-mail: ssakthivel@arci.res.in).

I. INTRODUCTION

THE 21st century has seen a significant evolution in various technologies in the field of solar energy conversion. There has been a rapid growth in photovoltaic device conversion technologies compared to that of solar thermal technology. Recently, solar thermal technology has attracted a substantial renewed interest due to its diversity and compatibility in various applications. The spectrally selective absorbing coating is a critical component in a solar thermal system which converts solar radiation into heat with minimal thermal losses. Development of spectrally selective absorbing coatings (SSACs) [1] for efficient conversion of solar energy was initially adopted in the 1970s [2]-[5]. The developed energy is being utilized efficiently for various applications such as solar hot water, solar desalination, industrial heat process, solar heating/cooling, and power generation. The primary requirements for SSACs are low reflectance (α) in the wavelength region of 0.3–2.5 µm and high reflectance (ε) in the infrared (IR) region (>2.5 µm). It should also have excellent mechanical stability, high-temperature stability, and good corrosion resistance at operating temperature to maintain the efficiency of a system in the long term. Currently, the development of SSACs is focused on achieving high selective properties to increase the efficiency of the system. As a result, the reported SSACs exhibit low thermal stability & corrosion resistance and observed decrement of efficiency when the coatings were operated in a system for the long term. Hence, it has become one of the big challenges for the commercialization of SSACs. Apart from that, the development of absorber coatings by vapor deposition technique becomes another challenge, since the coatings were not cost-effective, and some of the coatings are enclosed in evacuated tubes to avoid the degradation. Utilization of vacuum evacuated glass tubes for the SSAC leads to more expensive systems. So, the development of SSACs should also align with a production of cost-efficient absorber coatings. In order to develop a cost-effective SSAC with excellent corrosion and thermal stability, several researchers used cost-efficient methods such as sol-gel process, chemical oxidation, thermal oxidation, and electrochemical deposition technique. The sol-gel method is simple and cost-effective. Coatings can be easily scaled up with dip coating technique. In this connection, Kaluza et al. [6] developed the $CuFeMnO_4$ absorber coatings with silica developed by sol-gel method showed a solar absorptance of α = 0.85 to 0.93, but the

World Academy of Science, Engineering and Technology
International Journal of Energy and Environmental Engineering
Vol:13, No:7, 2019

emittance of the coatings was too high (ε_T = 0.07–0.62). Later, emittance was decreased by replacing Fe with Co up to 0.05, but there was no information on corrosion and thermal stability [7]. Another research group [8] reported the CoCuMnOx absorber coating on Aluminum substrate with an excellent solar absorptance of (α)=0.85–0.91, and thermal emittance (ε)<0.036 at room temperature. However, thermal and corrosion resistance of developed coatings has not been reported. Martin et al. [9] reported Cu–Co–Mn–Si–O based multi-layered coatings with a solar absorptance of 0.95 and emittance of 0.12 and developed coatings on a 1-meter substrate with the thermal stability of 360 °C, but there was no information on weather stability of the coatings. Previously, we reported Mn-Cu-Co-Ox-ZrO2[10] based absorber coating with optical properties (α=0.97, ε=0.17) by sol-gel method. We also reported absorber coating by thermal oxidation method with optical properties (α=0.91, ε=0.19 at 500 °C) [11]. However, both coatings reported with unsatisfactory thermal emittance. Apart from sol-gel, chemical oxidation method can be used to develop high selective absorber coatings with excellent uniformity. It is a simple, low-cost method and has the potential to upscale coatings at the required length. Initially, V. C. Sherma [12] reported absorber coatings by chemical oxidation method. However, they have obtained very low optical properties (α=0.38, ε=0.15). Similarly, C. S. Uma [13] also reported coatings on Stainless steel by chemical conversion with 0.91 of solar absorptance and 0.12 of emittance. However, there was no report on corrosion and thermal stability of developed coatings. Previously, we have also developed absorber coatings [14] on low-cost SS 202 with excellent optical properties (α=0.95, ε=0.17) for Organic Ranking Cycle (ORC) based solar thermal applications by chemical oxidation method. We upscaled coatings successfully up to 0.5 meters with targeted optical properties. The scalable SSACs technology which can be operated in an open-air atmosphere with high selectivity along with good thermal and corrosion resistance would be an excellent choice for solar thermal power applications.

In this regard, we have designed and developed the novel tandem absorber coating technology by low-cost methods. The developed coating has the potential to achieve cost-effective energy conversion with good optical properties, excellent thermal stability, and high corrosion resistance. Apart from that, we report the synthesis of coating sols in bulk level and upscaling of coatings up to 1 meter with required optical properties to fabricate a prototype receiver tube.

II. EXPERIMENTAL SECTION

A. Materials Used for the Development of Tandem Absorber Coatings

Commercially available stainless steel 304-grade substrates were used as a substrate to develop the absorber coatings. All reagents used for the synthesis of sols were purchased commercially and used without any further modification. To develop the composite oxide absorber layer, we have purchased Sodium dichromate dihydrate (99%), Sulphuric acid (98%) from Merck. For the preparation of tandem layer 1 (ZrO_2-SiO_2 layer on composite oxide layer) and tandem layer 2 (MgF2 AR layer on tandem layer 1), we have chosen Zirconium n-propoxide (70% in n-propanol), 3-glycidoxypropyl trimethoxisilane (GPTS, 97%), 2-isopropoxyethanol (99%), Isopropylalcohol (99%), n-propanol (99.5%), magnesium fluoride hydrate (87%) was obtained from Alfa Aesar.

B. Substrate Preparation

The absorber films were coated on a smooth and specular SS 304 polished substrates with an optimum roughness in the range of 0.05 μm to 0.10 μm. The dimensions of plates were 50 mm (Length) x 30mm (Width) x 1.5 mm (thickness). Initially, they were treated with ultrasonic waves in a bath filled with solvent to remove the greasy marks and metal dust particles. Then, substrates were rinsed carefully in ethanol and dried by blowing with the hot air gun subsequently blown with compressed N_2 gas.

C. Development of Composite Oxide Layer on SS 304 Substrates

The composite oxide absorber coating was developed by controlled chemical bath reactor with optimized temperature and chemical bath of 1 M concentrated sodium dichromate dissolved in a mixture of sulphuric acid and deionized water (3:5) solution as reported elsewhere [14]. In this process, the immersion of sample time is varied to obtain the composite oxide coating with good solar absorption property. Depending on the immersion time, there would be a variation of optical properties, which can be identified by the visual appearance of the coated substrate. After the development of composite oxide layer on the substrate, coatings were washed thoroughly with distilled water and wiped with a soft cotton cloth using an organic solvent. The cleaned absorber layer developed on the SS substrate was then dried by a hot air gun for 2-5 min.

D. Development of ZrO2-SiO2 Layer for Tandem Layer 1

To enhance the optical properties, we deposited a ZrO_2-SiO_2 layer over on a composite oxide layer. The overall stack termed as tandem layer 1. The development of the sol and coating procedure are described elsewhere [13]. The thickness of the ZrO_2- SiO_2 layer optimized by varying the withdrawal speed by using dip coater to obtain the high optical properties and optimum speed found out to be 1 mm/sec.

E. Development of MgF2 AR Layer for Tandem Layer 2

An ultra-low refractive index layer made of MgF_2 nanoparticles was applied over on a tandem layer 1 to enhance the absorption of the light over on the surface. The overall stack with MgF_2 layer termed as tandem layer 2. The synthesis of MgF_2 nanoparticles and preparation of AR coating sol was done as reported elsewhere [15]. The prepared sol was used to obtain a uniform thin film on a tandem layer 1 using the dip coating method. To obtain maximum optical properties, the thickness of the MgF_2 AR layer was optimized and observed high solar absorptance at an optimum withdrawal speed of 1 mm/sec.

World Academy of Science, Engineering and Technology
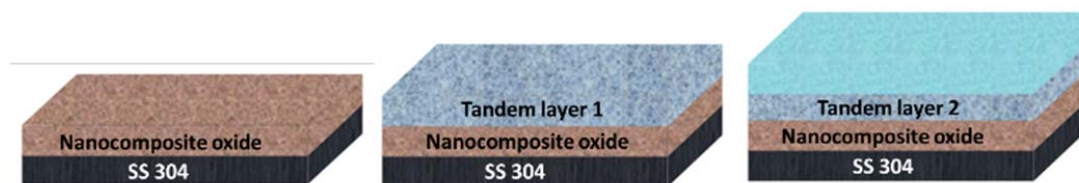International Journal of Energy and Environmental Engineering
Vol:13, No:7, 2019

Fig. 1 Schematic diagram of the compositeoxide layer on substrate, tandem layer 1 (ZrO_2-SiO_2/ Composite oxide layer/Substrate) and tandem layer 2 (MgF_2/ZrO_2-SiO_2/Composite oxide layer/substrate)

F. Characterization Techniques

The optimized coatings (composite oxide layer, tandem layer 1 and 2) were characterized by Carry Varian 5000 UV–Vis-NIR spectrophotometer to determine the optical reflectance. Thermal emittance of coatings was measured by FT-IR accessorized with blackbody and high-temperature cell provided by Bruker Optic GmbH. Thermal emissivity of coatings at different temperatures were calculated as explained in our earlier work [14]. Spectral emittance of absorber and AR samples was measured by Handheld Emissometer (Surface Optics) at room temperature. The scanning electron microscope (Carl Zeiss EVO 18) is employed to analyze the microstructure of all developed coatings. To determine the thickness, focused ion beam (FIB) milling was done using a Carl- Zeiss dual beam system (Neon-40) with Ga as the ion source and later cross-sectional images were taken. In addition, Spectroscopic ellipsometer (J. A. Woollam, USA, and Model: M-2000V) used to measure the thickness and refractive index of coatings.

III. RESULTS AND DISCUSSION

A. Optical Properties of the Composite Oxide Layer, ZrO_2-SiO_2 and MgF_2 AR Layer

The optical properties of composite oxide layer developed by chemical oxidation, tandem layers on composite oxide layer like ZrO_2-SiO_2 and MgF_2 AR layers were measured by using UV-Vis-NIR and FTIR spectroscopies. The reflectance spectra of the composite oxide layer, tandem layer 1 and 2 are represented in Fig. 2 (a) and thermal emissivity spectra in the IR region represented in Fig. 2 (b). The corresponding optical properties of all the developed layers were tabulated in Table I. The nanocomposite absorber layer was developed by immersing bare SS 304 substrate in a chemical bath. The process parameters such as sol composition, temperature, and process duration were optimized to get best optical properties. At an optimized duration, the substrate got oxidised and formed a nanocomposite oxide layer on the substrate; the coating exhibited 80% of absorption and 11% of thermal emissivity as shown in Fig. 2.

To further enhance the optical properties, ZrO_2-SiO_2 layer has been developed on composite oxide absorber layer. The optimized thickness and reduced refractive indices make the tandem layer 1 selective through the destructive interference of waves between the two interfaces of the coating. The tandem layer 1 exhibited the 0.92 of absorptance and 0.12 of

thermal emissivity. Finally, an antireflective (AR) layer with low refractive index coating of MgF_2 applied on the tandem layer 1 for further improvement of the solar absorptance. The ultra-low refractive index layer on a tandem layer 1 diminished the reflectance in UV region to obtain the 0.94 of solar absorptance and 0.14 of thermal emissivity.
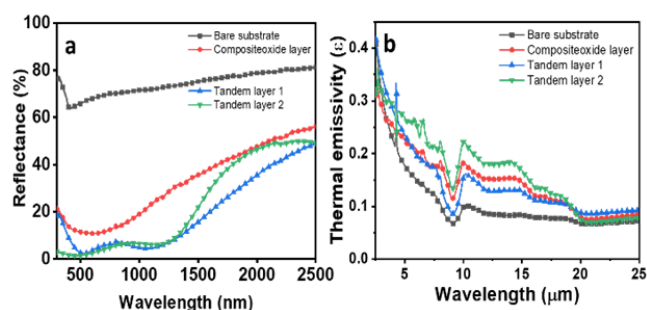

Fig. 2 (a) Reflectance spectra and (b) thermal emissivity spectra of composite oxide layer, tandem layer 1 and 2

TABLE I
OPTICAL PROPERTIES OF THE COMPOSITE OXIDE LAYER, TANDEM LAYER 1 AND 2

Symbol	Solar absorptance (α)	Thermal emissivity (ε)
Bare substrate	0.32	0.11
Composite oxide layer	0.80	0.12
Tandem layer 1	0.92	0.13
Tandem layer 2	0.94	0.14

B. Morphological Study of the Composite Oxide Layer, Tandem Layer 1 and 2

The developed coatings were studied by FESEM to understand the morphology of coatings to identify the reason behind the excellent optical properties. Fig. 3 represents the morphology of the composite oxide layer tandem layer 1 and 2.

From Fig. 3, we can observe that the developed composite oxide absorber comprises of a uniform layer without any cracks, and it comprises of nanopores having a size in the range of 18 to 22 nm. These pores can help in increasing the absorption by reducing the multiple reflections across the surface of the composite oxide absorber layer. The tandem layer 1 exhibits a uniform ZrO_2-SiO_2 layer without any cracks and whereas tandem layer 2 comprises of MgF_2 nanoparticles with good uniformity. The average particle size was found out to be 15 nm.

World Academy of Science, Engineering and Technology
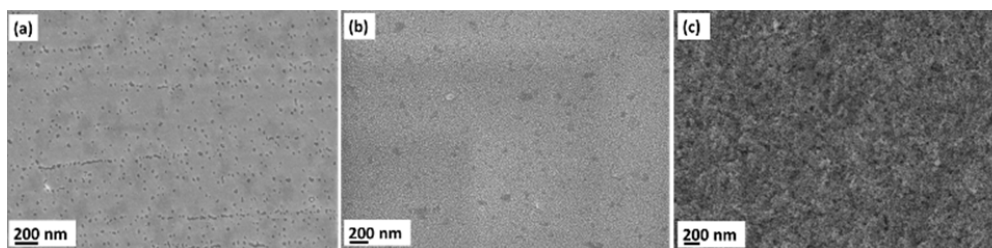International Journal of Energy and Environmental Engineering
Vol:13, No:7, 2019

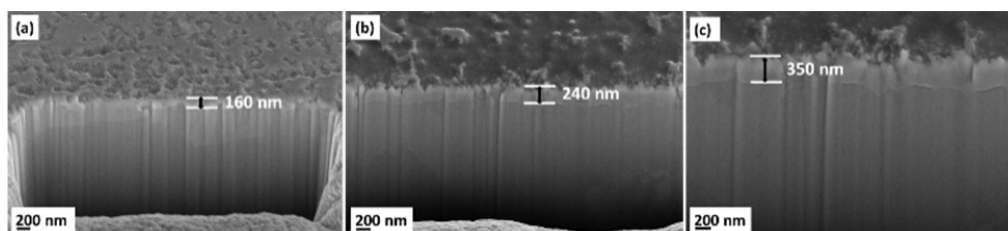Fig. 3 Morphology of (a) composite oxide layer, (b) tandem layer 1 and (c) tandem layer 2

Fig. 4 The thickness of (a)composite oxide layer, (b)tandem layer 1 and (c)tandem layer 2

C. Thickness Study of the Composite Oxide Layer, Tandem Layer 1 and 2 by FIB and Ellipsometer

The developed coating thicknesses were estimated by FIB and ellipsometer, and the refractive indices were estimated by ellipsometer.

To determine the thickness of the optimized coatings through FIB, the coatings were milled for a particular area using an ion beam assistance and the cross-sectional images were taken by the SEM at angles of 36° with respect to the film surface. Fig. 4 represents the cross-sectional images of composite oxide layer, tandem layer 1 and 2. The tandem layer of SSAC with all three layers of coatings is 350 ±5 nm. From the figure, we can observe the thickness of a composite oxide absorber layer is found out to be 160±5 nm, whereas ZrO_2-SiO_2 layer deposited on a compositeoxide absorber layer is 80±5 nm, as shown in Fig. 4 (a) and (b) respectively. The thickness of MgF_2 AR layer on ZrO_2-SiO_2 layer is found to be 90±5 nm. To estimate thickness and refractive index of deposited films, experimental data were measured for developed films and then modelled a suitable mathematical function. Finally, we simulated spectra fitted with experimental spectra to get low mean square error. The thickness and refractive index values of the composite oxide layer are around 150 ± 5 nm and 2.10 ± 0.01, ZrO_2-SiO_2 layer: 90 ± 5 nm and 1.59 ± 0.01, MgF_2 AR layer: 80 ± 5 nm and 1.31 ± 0.01, respectively, and values are mentioned in Table II. The multilayer stack with refractive index gradient has led to a 95% of absorption.

TABLE II
THICKNESS AND REFRACTIVE INDEX VALUES OF COMPOSITE OXIDE LATER AND TANDEM LAYER 1 AND 2 THROUGH FE-SEM AND ELLIPSOMETER

Layer type	Thickness (nm)		Refractive index
	FESEM	Ellipsometer	
Compositeoxide layer	160	152	2.10
Tandem layer 1	80	85	1.59
Tandem layer 2	90	89	1.31

D. Thermal Stability and Corrosion Resistance of Developed Coatings

1. Thermal Stability Study

The coatings were subjected to thermal stability test to determine the durability of coatings at that particular temperature. The samples were subjected to a temperature of 250 °C for up to 100 h. Each thermal cycle consists of 2 h heating to attain 250 °C, 2 h soaking duration, and 5–6 h cooling to attain the room temperature. After completion of every cycle, samples were measured for optical properties to determine the degradation. Based on tests conducted, it is evident that the developed nanocomposite oxide, tandem layers 1 and 2 are thermally stable up to 100 cycles at 250 °C.

2. Corrosion Resistance Study

Developed coating were subjected to salt spray test to evaluate the corrosion resistance. According to ASTM B117, 5% NaCl solution was used to generate vapours at 35 °C/min in a salt spray chamber. Samples were characterized, after every 24 hours (one cycle) to determine the change in the optical properties. The composite oxide layer, tandem layers 1 and 2 exhibited the excellent corrosion resistance in salt spray test and found to have no change in the optical properties until 200 h. Based on the tests (Thermal and corrosion) conducted, it is evident that the developed coatings have excellent corrosion resistance and thermal durability up to 250 °C.

IV. DEVELOPMENT OF TANDEM SOLAR ABSORBER COATINGS ON PRODUCTION SCALE

After the development of a tandem absorber layers successfully in lab level with excellent optical properties (α = 0.95, ε = 0.14), we have focused on development of coatings for prototype level for 1-meter length substrates. We designed and procured custom made chemical bath reactor and dip coater, which have the capability to develop coatings up to 1-meter size (as shown in Fig. 5. 50 liters of 1 M sodium

World Academy of Science, Engineering and Technology
International Journal of Energy and Environmental Engineering
Vol:13, No:7, 2019

dichromate salt solution was prepared as described in earlier in the experimental section (Section 2.1) for chemical bath reactor. One-meter length SS 304 tube was cleaned by using ultrasonicater and then immersed in chemical bath reactor for an optimized duration to form a composite oxide layer. To develop multilayer stack over on the composite oxide layer, 6 liters of ZrO_2-SiO_2 and MgF_2 antireflective sol were prepared by sol-gel and nanoparticles dispersion method, respectively. Later, coatings were deposited on 1-meter long SS 304 tube using dip coating system with an optimized withdrawal speed and followed by curing in Memmert oven at 250 °C. The developed prototype one-meter absorber tube has good optical properties, excellent uniformity and scratch resistance as shown in Fig. 5 (c). We have successfully demonstrated the absorber coatings from lab to prototype scale in a cost-effective manner with targeted properties. The cost-effective technology has attracted many industries of low and medium temperature CST business in India. Recently, the cost-efficient receiver tube technology is transferred to an Indian industry, GreenEra India Pvt. Ltd.

Fig. 5 (a) Chemical bath reactor (b) Dip coater and (c) ARCI's indigenously developed 1m receiver tube

V. CONCLUSION

In CST, cost-efficient receiver tube is one of the key elements to make the technology more viable in terms of efficiency and economics. Hence, we have focused on cost-effective absorber coating technology by tandem absorber layers approach on SS 304 substrate with a chemical oxidation, sol-gel, and nanoparticle coating methods. The effective usage of low refractive index multilayer stack has led to excellent optical properties to achieve 95% of absorption and 14% of emittance with excellent corrosion and thermal stability up to 250 °C. The synthesis of sol is simple, and coatings are scalable at even large scale at low cost with a facile dip coating process. We successfully prepared a one-meter prototype receiver tube with excellent uniformity and scratch resistance. The technology has a superior advantage of easy scalability to industry level and a breakthrough for low and medium temperature CST business. Recently, the prototype demonstrated technology has been tr transferred to GreenEra India private limited for CST process heat applications.

REFERENCES

[1] O.P. Agnihotri, B.K. Gupta, Solar selective surfaces, first ed., A Wiley Interscience publication, New York, 1981.
[2] H.G. Craighead, R.A. Buhrman, "Optical-properties of selectively absorbing Ni-Al_2O_3 composite films", Appl. Phys. Lett. 31 (1977) 423–425.
[3] B.O. Seraphin, "Chemical vapor deposition of thin semiconductor films for solar energy conversion", Thin Solid Films 39 (1976) 87–94.
[4] W.F. Bogaerts, C.M. Lampert, "Materials for photothermal solar energy conversion", J. Mater. Sci. 18 (1983) 2847–2875.
[5] C.E. Kennedy, Review of Mid- to High-Temperature Solar Selective Absorber Materials, NREL/TP-520-31267, National Renewable Energy Laboratory, Golden, CO, 2002.
[6] L. Kaluza, A. SURCA-vuk, B. Orel, "Structural and IR spectroscopic analysis of sol-gel processed $CuFeMnO_4$ spinel and $CuFeMnO_4$/silica films for solar absorbers", J. Sol.- Gel Sci. Technol. 20 (2001) 61–83.
[7] L. Kaluza, B. OrelL, G. Drazic, M. Kohl, "Sol – gel derived CuCoMnOx spinel coatings for solar absorbers: structural and optical properties", Sol. Energy Mater. Sol. Cell. 70 (2001) 187–201.
[8] J. Vince, A. Šurca Vuk, U. Opara Krašovec, B. Orel, M. Köhl, M. Heck, "Solar absorber coatings based on CoCuMnOx spinels prepared via the sol-gel process: structural and optical properties", Sol. Energy Mater. Sol. Cells 79 (2003) 313–330.
[9] Joly, Y. Antonetti, M. Python, M. Gonzalez, T. Gascou, J.L. Scartezzini, A. Schüler, "Novel black selective coating for tubular solar absorbers based on a sol-gel method", Sol. Energy 94 (2013) 233–239.
[10] M.S. Prasad, B. Mallikarjun, M. Ramakrishna, J. Joarder, B. Sobha, S. Sakthivel, "Zirconia nanoparticles embedded spinel selective absorber coating for high performance in open atmospheric condition", Sol. Energy Mater. Sol. Cells 174 (2018) 423-432.
[11] A. Srinivasa Rao, S. Sakthivel, "A highly thermally stable Mn–Cu–Fe composite oxide based solar selective absorber layer with low thermal loss at high temperature", Alloys Compd., 644 (2015), 906-9151.
[12] V.C. Sharma, A. Sharma, P. Ilenikhena, "Chemical oxidation and spectral selectivity of Austenitic stainless steel AISI 321(For use in solar-Energy Application)", Energy 13 (1988) 749–754.
[13] C.S. Uma, L.K. Malhotra, K.L. Chopra, "spectrally selective surfaces on stainless steel produced by chemical conversion", Thin Solid Films 147 (1987) 243–249.
[14] M. Shiva Prasad, K. Chandra Sekhar Reddy, S. Sakthivel, "Development of cost-efficient solar receiver tube with a novel tandem absorber system", Appl. Therm. Eng. 109 (2016) 988–996.
[15] D. Karthik, S. Pendse, S. Sakthivel, E. Ramasamy, S.V. Joshi, "High performance broad band antireflective coatings using a facile synthesis of ink-bottle mesoporous MgF_2 nanoparticles for solar applications", Sol. Energy Mater. Sol. Cells 159 (2017) 204–211.