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Nanocoatings - designed layers for solar thermal applications

ABSTRACT

Solar energy is one of the most used renewable energy source in different applications nowadays. The direct method of harnessing solar energy is the solar thermal conversion method using solar absorbers.

Solar thermal collectors are mainly used for heating water and for space heating. They capture incident solar radiation, convert it to usable thermal energy, and transfer the solar energy into a heat transfer fluid. All of these requirements should be accomplished economically with a minimum energy loss. One of the most important components of the solar thermal collector is the solar absorber. To be effective, the absorber should exhibit wavelength selectivity, i.e. have maximum solar absorbance, minimum solar reflectance and thermal infrared emittance. A high solar absorbance is required to collect as much of the incident solar radiation as possible and a low thermal infrared emittance contributes to minimize radiant energy losses. Usually, lightweight materials like, copper or aluminium, that have a high thermal conductivity, are used to transfer the absorbed energy from the surface to the media (fluid) which has to be heated.

For high coefficient of efficiency of solar thermal collectors, the most important parts are: 1) spectral selective coatings that are composed of islands of metal embedded in a three-dimensional matrix of dielectric with a solar absorbance of $\alpha > 0.95$ and an emittance of $\varepsilon \leq 0.05$. Usually, those are TiN_xO_y coatings made by Physical Vapour Deposition (PVD) process, e.g. by combination of magnetron sputtering and cathodic arc evaporation deposition; and 2) enhanced construction solutions for better solar heat transmission from the absorber surface to the medium using the different absorbers' designs.

In this context, the solar selective coatings are very important item on the absorbers' surface. They have advantages compared to galvanic or sprayed coatings used in solar applications. Their proper design and optimisation of layers order in multilayered structure of the coating and thickness dimensions of each layer is very important. Namely, transformation of solar irradiance to heat and transfer the heat from selective coating to the substrate materials such as: Cu, Al, Stainless steel, glass or polymers is very important step and it differ from substrate to substrate. Usually, these coatings are with thickness of several hundred nanometres, and each layer is with specific functional role within the coating. The general composition of selective coating consists of: protective layer, antireflective layer, several absorbing layers like, cermet layers, diffusion layer and infra red reflective layer.

The main focus of this paper is optical properties of nanocoatings based on PVD selective coatings which allow maximum absorbance, minimum emittance and as much as possible efficiency of the solar thermal collector that is assembled with coated absorbers with selective coatings.

Keyword: Nanocoatings, solar thermal collectors, solar energy, design.

1. INTRODUCTION

Photothermal utilization of solar energy typically involves a solar heating system that produces

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hot water or space heat. The heart of the solar hot water or space heat. The heart of the solar heating system is the solar collector. In order to enable effective solar energy utilization, absorption of incident solar radiation should be maximized and thermal losses from the collector minimized. The solar absorbing surface is one of the key components of a solar collector, and its optical properties and quality influence both the heat losses and gains. [1]

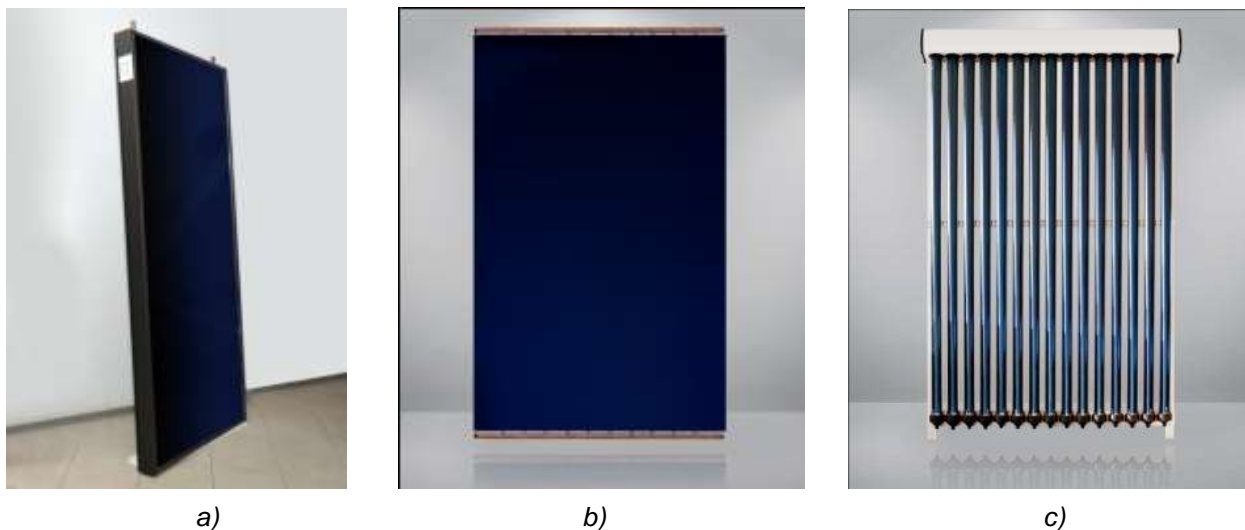


Figure 1 - a) Flat plate collector, b) absorber for flat plate collector, c) vacuum tube collector (photos made by Camel Solar collectors -Skopje, Macedonia) [1,2]

High absorptance and low emittance accompanied with economical manufacturing cost, large production volumes and long-term durability of solar products are often the key driving factors of the industrial development work on solar thermal absorbers and they are discussed in this work [1,2].

1.1. Spectrally Selective Absorber Surfaces

The standard spectral solar flux incident at the surface of the earth, after atmospheric absorption, is limited to the range between 0.3 and 2.5 μm i.e. UV/Vis/NIR wavelength ranges. Our eye is sensitive only to the visible part of the solar spectrum.

Figure 2 shows the hemispherical solar irradiance that reaches the surface of the earth after passing the atmosphere during clear sky conditions. [This is adapted from the International Organization for Standardization (ISO) 20 for air mass 1.5 (AM1.5) i.e. when the sun is about 42° above the horizon. The spectrum consists of direct and diffuse radiation and both fluxes contribute to heat-up flat plate solar collectors.]

The blackbody spectrum for temperatures between 50° to 100°C and the solar spectrum do not overlap in any wavelength range, as was shown in Figure 2. It is, therefore, possible to design a surface which absorbs the maximum possible of the incident solar radiation, but does not re-emit the absorbed energy. A material having high absorbance (low reflectance) in the solar spectrum and low emittance (high reflectance) in the thermal infrared is called a selective solar absorber. An ideal spectrally selective surface should have a reflectance of zero in the solar wavelength range and unity in the thermal infrared. For temperatures below 100°C the on-set

wavelength for the low to high reflectance is about 3 μm and for higher temperatures ($\approx 300^\circ\text{C}$) the critical wavelength is around 2 μm (Figure 2).

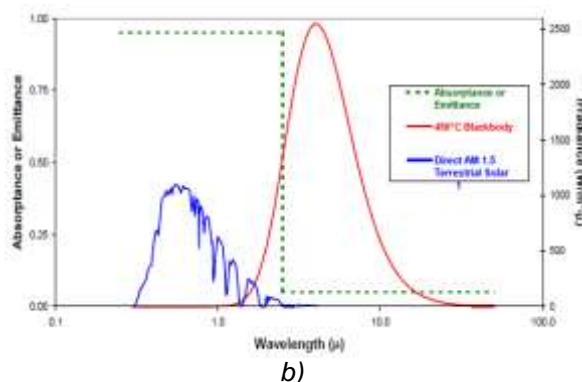
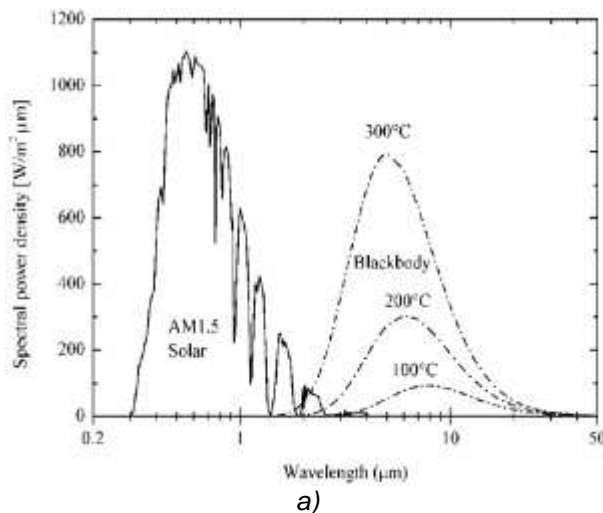


Figure 2 - a) Solar hemispherical spectral irradiance for air mass 1.5 and blackbody spectral emittance at 100°C, 200°C and 300°C; b) Spectral performance of an ideal selective solar absorber [3]

A spectrally selective absorber has different spectral reflectance at different wavelengths. The ideal spectrally selective surface operating at below approximately 100°C has as zero reflectance (i.e. unity solar absorptance) between 0.3 and 2.5 μm and a unity reflectance (i.e. zero thermal emittance) between 2.5 and 50 μm. Unfortunately, an ideal surface does not exist in nature, nor can it be

manufactured because no known combination of materials exhibits ideal behaviour in the reflectance transition wavelength range (Figure 2) [3].

Figure 3 reports a variety of selective coatings and surface treatments for better solar selective absorptance [3].

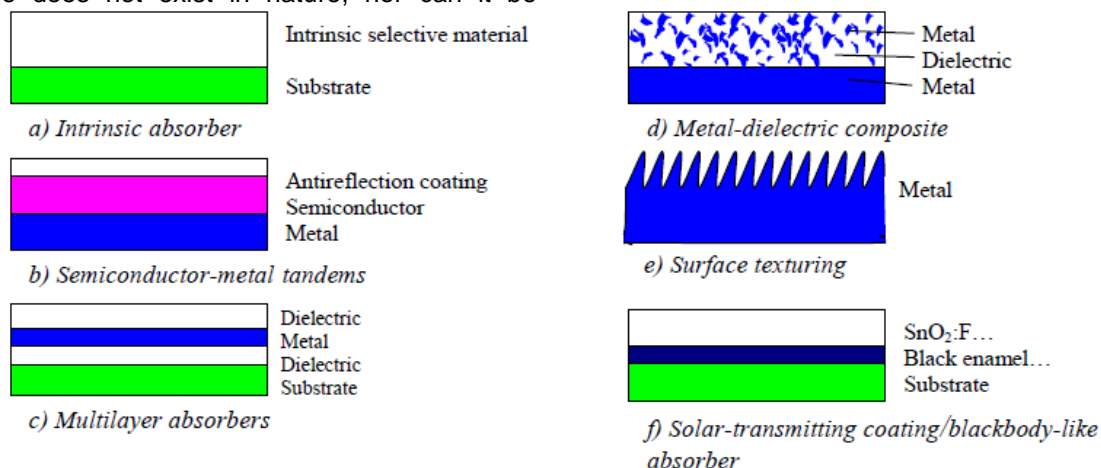


Figure 3 - Different designs of coatings and surface treatments for selective solar absorption [3]

The highly absorbing metal-dielectric composite, or cermet, consists of fine metal particles in a dielectric matrix, or a porous oxide impregnated with metal. These films are transparent in the thermal IR region, while they are strongly absorbing in the solar region because of inter-band transitions in the metal and the small particle resonance. When deposited on a highly IR reflective mirror, the tandem forms a selective surface with high solar absorptance and low thermal emittance. The metal-dielectric concept offers a high degree of flexibility, and the solar selectivity can be optimised by proper choice of constituents, coating thickness, particle concentration, size, shape, and orientation. The solar absorptance can be boosted with a suitable choice of substrates and

AR layers, which can also provide protection (for example, from thermal oxidative degradation).

TiN_xO_y film possess excellent absorptance towards visible light, in which most of solar energy lies, and good transmittance for the infrared. This new “blue” coating, based on titanium, marked a significant increase in performance and represented the first environmentally friendly alternative to the so far commonly used “black-chrome”- and “black-nickel-coatings” (Figures 4 and 5).

Nowadays, a variety of techniques exist for selective surface coatings, such as: vacuum evaporation, vacuum sputtering, ion exchange, chemical vapor disposition, chemical oxidation, dipping in chemical baths, electroplating, spraying, screen printing and brass painting method, etc[4].

Absorption And Emissivity Values For Flat-Plate Collector Coatings

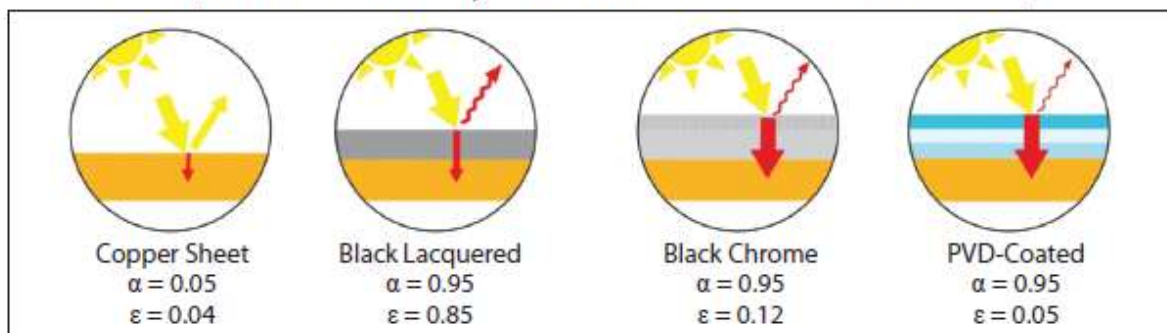


Figure 4 - Comparison of absorbers' surfaces that are selectively coated with different methods [source: Alanod Solar]

Different techniques for deposition of selective coatings on absorbers surfaces produce different optical performance of the coated surfaces. For example, Fig. 4 compares basic optical properties of surfaces that are selectively coated with different techniques, while Fig. 5 compares collector's efficiency assembled with different types of absorbers.

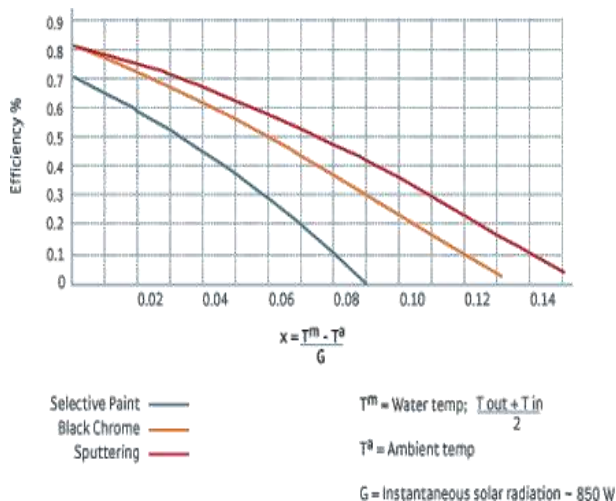


Figure 5 - Collector efficiency with selective painted, black chrome and sputtering coated absorbers

Spectrally selective coatings which are stable up to temperatures ≤ 300 °C (in air and vacuum) have been developed in the past. These coatings are mainly deposited from wet chemical routes (e.g., electrodeposition) and have been reviewed widely in the literature [3, 4].

Because of the environmental issues as well as low thermal stability of these wet chemical deposited coatings, researchers all over the world started looking for other alternative routes such as physical vapor deposited (PVD) coatings.

1.2. Physical Vapor Deposition

PVD techniques range over a wide variety of applications from decorative, to high temperature superconducting films. A very large number of inorganic materials: metals, alloys, compounds, and mixtures as well as organic materials (e.g. polymers) can be deposited using PVD technologies. Nowadays, PVD is used to form multilayer coatings, gradient-depositions, or very thick deposits [5 - 7].

PVD processes include a wide range of vapour-phase technologies. In general, PVD is used to describe variety of methods to deposit thin solid films by the condensation of a vaporized form of the solid material onto various surfaces. PVD process involves physical ejection of material as atoms or molecules and condensation and nucleation of these atoms onto a substrate. The

vapor-phase material can consist of ions or plasma and is often chemically reacted with gases introduced into the vapour, called reactive deposition, to form new compounds. The thicknesses of deposited layers could be from few nanometers to thousands of nm [8]. The process is characterized by two sets of parameters: a) plasma that includes the electron density, electron energy, and ion distribution, and b) process parameters which include evaporation/sputtering rate, gas composition, pressure, gas flow rate, substrate bias, and temperature. The main categories of PVD process are [7]:

- vacuum deposition* (evaporation) - material from a thermal vaporization source comes to the substrate with little or no collision with gas molecules in the space between the source and substrate;
- sputter deposition* - deposition of particles vaporized from a surface "target" by the physical sputtering process. This is a non-thermal vaporization process where surface atoms are physically ejected from a solid surface by momentum transfer from an atomic-sized energetic particle that bombard the surface (usually it is a gaseous ion, accelerated from a plasma). Generally, the source to-substrate distance is short compared to vacuum deposition;
- arc vapor deposition* - uses a high current, low voltage arc to vaporize a cathodic electrode or anodic electrode and deposit the vaporized material on the substrate. The vaporized material is highly ionized and usually the substrate is biased so as to accelerate the ions ("film ions") to the substrate surface. Usually, arc vapour deposition is used to deposit hard and decorative coatings;
- ion plating* - utilizes periodic bombardment of the depositing film by atomic-sized energetic particles to modify and control the properties of the depositing film.

The deposition process must be chosen to fit the required properties and the final application. *Hybrid processes* usually combine the best attributes of each PVD and/or non-PVD processes like, CVD (chemical vapour deposition) process. They are now being used for creating advanced thin film materials and structures that were not possible with conventional techniques decades ago [5-8].

In this work, physical vapour deposition (PVD) as method for surface modification and selective coating deposition on polymeric composite and glass solar thermal absorber is described. The method is eco-friendly. At the same time, this is a good opportunity to replace metallic solar thermal

collectors based on Cu or Al absorbers with polymer or glass materials that will be deposited with proper selective solar coatings.

2. EXPERIMENTAL

2.1. Materials

Selected polymers and glass tubes are substrate materials chosen for this study. Namely, polymer compositions based on graphite-doped PC (Figure 6a) and borosilicate glass tubes (Figure 6b) are selected [9-13].

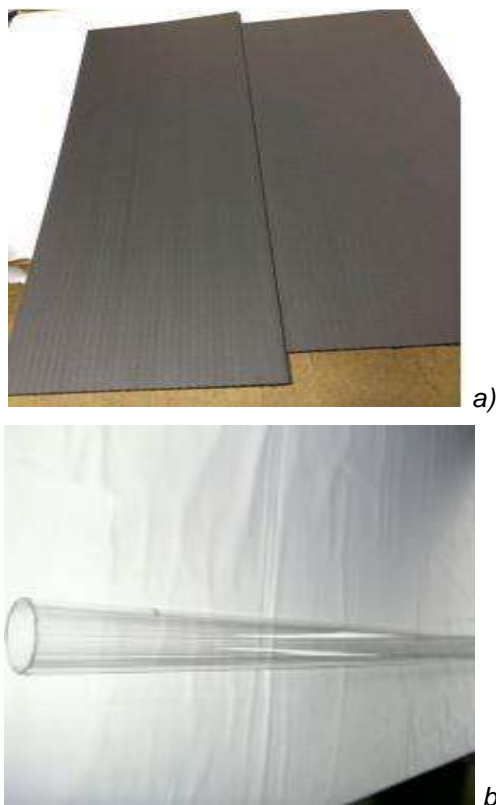


Figure 6 - Raw solar absorber made of: a) graphite-doped polycarbonate, b) glass borosilicate tube

2.2. Method of deposition

PVD technique was used for deposition of solar selective coatings. Namely, PVD chamber - VU 1100 (Plasma -Center for plasma technologies-Skopje, Macedonia) is used, presented in Fig.7.

The coating procedure consists of several steps in PVD chamber for both type of materials that in general are:

- surface preparation (plasma cleaning, etching, and chemical modification of the surface), and
- PVD deposition of multi-layered set of coatings.

Depending on type of substrate materials each of these steps could vary in terms of cleaning, different activation of the surface, modification, and deposition time.



Figure 7 - PVD chamber (VU 1100) in Plasma facility

3. RESULTS AND DISCUSSION

3.1. Selective coating suitable for polymer

Figure 8a) presents an image of coated polymer absorber (graphite-doped PC) while Fig. 8b) presents the scheme of composition of the selective coating on polymer substrate. Fig. 8c) obtained by scanning electron microscopy (SEM) confirms multilayered structure of the selective coating with total thickness of ~600 -700 nm. [11,14].

The process of coating deposition involves an appropriate bonding layer between coatings and the base substrate material (polymer composition). Each of the layers is with a specific role/function in specified absorber profile.

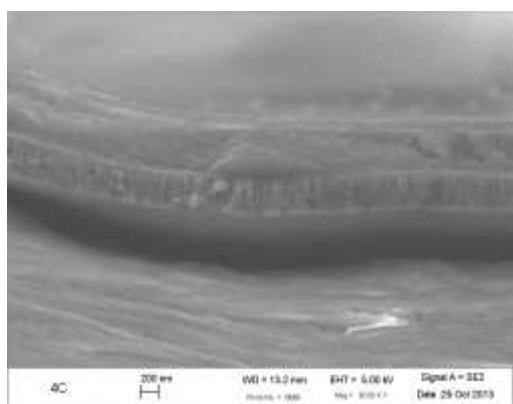
The first or interface layer is the layer that needs to establish the connection (adhering) between the substrate polymeric material and the next multilayered coating. Usually, it can be made by plasma activation step-etching in PVD chamber (Fig.7) with different working gasses. *The second layer is IR reflector layer* is PVD deposited Cu layer that reflect the IR radiation from the fluid in the absorber channels. *The third and forth layers are cermet TiOxNy layers (high metal fraction and low metal fraction)*, followed by *the fifth one that is TiO₂*. The last TiO₂ /SiO₂ layer possess antireflective (AR) properties, and actually this layer is a good base for placing the *final protective / AR layer*.

The double *cermet* (CERAmic – METAl) absorbing layers (actually, the third and fourth layers) are metal-dielectric composite layer transparent in the thermal IR region (3- 25) μm , while it is strongly absorbing in the solar region (0.3 -2,5) μm due to its interband transitions in the metal and the small particle resonance. Thermal emittance strongly increases with the thickness of the cermet increases due to NIR absorption. By reduction of the thick-

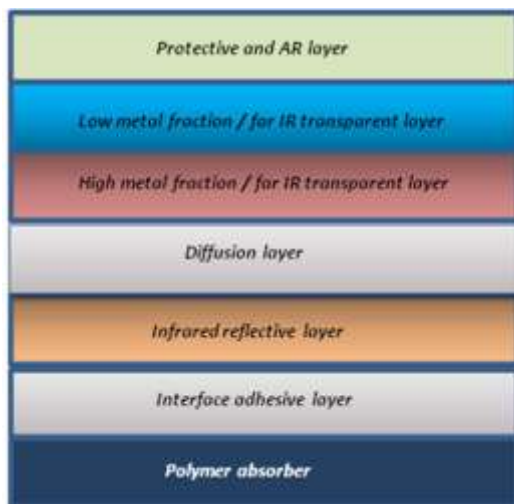
ness of cermet layer and increase of IR reflector layer, the emittance value can be reduced as well.



a)



b)



c)

Figure 8 - a) Photo of polymer absorber (two modular attached absorbers), b) composition of selective coating, c) SEM image of multilayered nanocoating on polymer composite absorber

The antireflective and protective layer achieved higher transmission and low reflectivity values for optimal optical performance. At the same time, they provide a good protection from weather and environmental conditions.

With this multilayered structure on polymer composite material, the selective coating is with maximal absorbance. The controlled emittance of the coated absorbers will allow use of them under different weather and exploitation conditions. In regions with high solar irradiation and high ambient temperatures, emissivity can be controlled (increased) without changing the absorbance with simply designing a proper selective coating on collector absorbers. And, contrary on this, if the solar radiation in particular region is low and low ambient temperatures exist, we can make coating with low emissivity values and maximal absorbance on the absorbers and harness as much as possible of the poor solar irradiation in those regions.

3.2. PVD Selective coating suitable for solar-thermal glass absorbers

In the case of solar glass absorbers, again the most important part is to achieve high absorption and low emission with PVD selective coating on them. Plasma [13] developed a low cost coating, high thermal stability that has a low thermal emittance for required temperatures.

As known, copper (Cu) or aluminum (Al) type absorbers are IR reflectors so to achieve high absorption and low emission it is only necessary to deposit absorption and antireflection layers. For glass absorbers, obtaining a surface with high absorption and low emission at working temperatures, it is necessary to change some layers within the multilayered coating from the standard PVD coatings on metals. In general, a functional coating over glass tubes consists of:

a) *Interface adhesive layer* is a good adhesive layer. It needs to have an excellent microstructure to achieve good bond quality, high thermal conductivity and cope with thermal stress variations.

b) *Double-CERMET absorbing layer* is composed of two cermet layers, a low-metal-volume fraction (LMVF) cermet layer placed on a high-metal-volume fraction (HMVF) cermet layer. The LMVF means that the dominant component is the ceramic part compared to the metal part of the cermet layer which means that in this layer the metal volume fraction is low. The HMVF means that the dominant component is metal compared to the ceramic part of the cermet layer which means that the metal volume fraction is high. Metal-dielectric composite or cermet layer is transparent in the thermal IR region ($3\div 25$) μm , while it is strongly absorbing in the solar region ($0.3\div 2,5$) μm because of interband transitions in the metal and the small particle resonance. Thermal emittance strongly increases as the thickness of the cermet increases due to NIR absorption. Reducing the

thickness and increasing the metallic concentration in the same proportion can reduce emittance.

c) *AR-antireflection layer* must enable high transmittance and must reduce the reflectance of the incident solar radiation. It should be emphasized here that in addition to this requirement the antireflection (AR) coating must be mechanically very tough, withstand drastic climatic and thermal variations. AR layer also affects towards minimizing

the optical interference effects within the film and to increase the solar absorbance by ~ 3-4%.

Thickness of each of the above mentioned layers depends on the optical characteristic of the respective layer. The absorption is around 95 % to 96% , emittance of ~ 6% and very high stability in working temperature is achieved within this project (Fig. 9) [13].

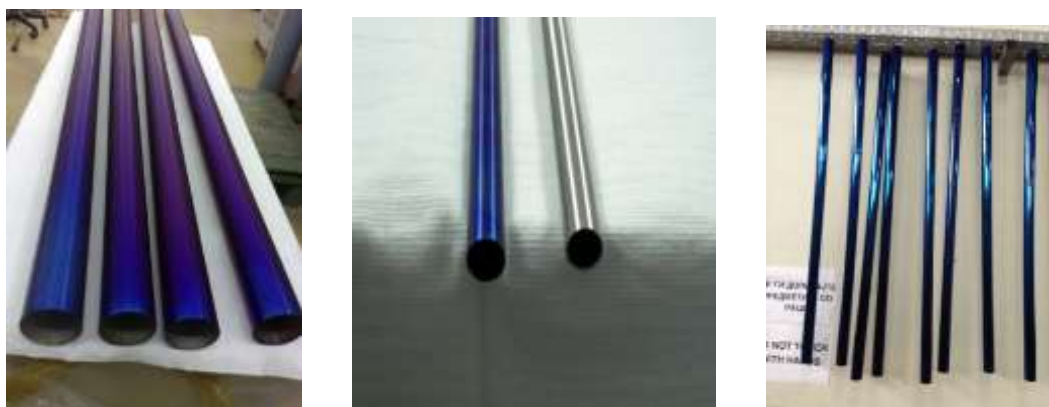


Figure 9 - PVD selective coatings on different glass tubes [13]

4. CONCLUSION

Nano PVD optical selective coatings over variety of absorbers are the most promising coatings for transformation of solar irradiation to heat within the solar thermal collectors.

The benefits of nano PVD selective coatings compared to galvanic black chrome and black paint coatings are multiple, the most important fact is that only several hundreds of nanometer thick PVD coatings allow fast and efficient transferring of the heat from the selective coating to the substrate and from the substrate (Cu, Al, Stainless steel, polymer or glass) to circulation fluid while stopping emission from fluid to ambient. Different substrate materials are used for solar thermal absorbers depending on application: low temperature, medium and high temperature absorbers. In general, polymer absorbers are used for low temperature application while metal and glass absorbers are used for low and medium temperature application. Stainless steel, titanium or similar materials are used for high temperature application.

Multilayered selective coatings on polymers and glass substrates explained in this work consists of several layers: protective layer, antireflective layer, absorbing layers, IR layer and interface adhesive layer, that all together have not only high absorbance (even more than 95%), also possess minimum emissivity (e.g. less than 5% for metal absorbers and 5 to 30% for polymer

absorbers), possess minimum reflectivity, but long term stability. The solar thermal collectors that include absorbers with multilayered selective coatings have very high efficiency.

5. REFERENCES

- [1] I.Nasov, M.Koehl, A.T.Petkoska (2014) Novel Type of Facade Window Collector-Double Benefits: Good Architectural Appearance of Facade and Solving the Problems of Long Term Stability / Efficiency, SHC 2013, Energy Procedia, 48, 1320-1325.
- [2] I. Nasov, A.T.Petkoska (2014) Solar energy in architecture - novel facade collectors, Tehnika, 69(1), 27-32.
- [3] C.E.Kennedy (2002) Review of Mid- to High-Temperature Solar Selective Absorber Materials, NREL/TP-520-31267.
- [4] N.Madhukeshwara, E.S.Prakash (2012) An investigation on the performance characteristics of solar flat plate collector with different selective surface coatings, International Journal of Energy and Environment, 3(1), 99-108.
- [5] R.F.Bunshah (2001) Handbook of hard coatings, Noyes Publication.
- [6] A.A.Tracton (2006) Coatings technology handbook, Taylor & Francis Group, LLC.
- [7] D.Mattox (2010) Handbook of Physical Vapor Deposition (PVD) Processing, Elsevier Inc.
- [8] P.Martin (2010) Thin Film Coatings, III-rd Ed., Elsevier Inc.
- [9] R.Ryntz, F.Yaneff (2003) Coatings of Polymers and Plastics, Marcel Dekker Inc.

- [10] R.Wells (1994) Surface engineering of polymers, Durham University, PhD Theses.
- [11] EU FP7 scheme of Research for SMEs: "Development of a modular, all-POLYmer SOLar thermal collector for domestic hot water preparation and space heating" (PolySol), Grant agreement No: 262149.
- [12] A.Trajkovska Petkoska, I.Nasov (2014) Surface engineering of polymers - Case study: PVD coatings on polymers, *Zastita materijala*, 55(1),3-11.
- [13] EU FP7- Research for SME associations: All glass mid temperature direct flow thermal solar vacuum tube (Soleglass), Project No: 285956.
- [14] I.Nasov, A.T.Petkoska, S.Fisher, D.Cartlidge (2014) Surface engineering of polymers - Case study: polymer solar thermal collector, International Conference on Industrial Tools and Material Processing Technologies - ICIT & MPT.

IZVOD

NANOPREVLAKE- DIZAJNIRANJE SLOJEVA ZA SOLARNE KOLEKTORE

Danas je solarna energija je jedan od najčešće korišćenih izvora obnovljive energije u različitim primenama. Direktna metoda kontrolisanja solarne energije, podrazumeva metodu njene konverzije u toplotnu energiju pomoću solarnih apsorbera. Solarni termalni kolektori, uglavnom se koriste za zagrevanje vode i za grejanje prostorija. Zarobljeno solarno zračenje, pri tome se pretvara u korisnu toplotnu energiju, kroz konverziju solarne energije u toplotnu energiju fluida. Takav proces mora biti ekonomičan, i uz što manji gubitak energije. Jedna od najvažnijih komponenti solarnog kolektora je toplotni solarni apsorber. Da bi bio efikasan, apsorber treba pokazivati selektivnost u odnosu na talasnu dužinu, odnosno treba da poseduje maksimalnu solarnu absorbtivnost, minimalnu solarnu refleksiju i toplotnu infracrvenu emisivnost. Visoka solarna absorbtivnost je neophodna da bi se prikupio što veći deo upadnog sunčevog zračenja, dok niska toplotna infracrvena emisivnost doprinosi da se minimizira gubitke energije zračenjem. Obično, lagani materijali poput, bakra ili aluminijuma, koji imaju visoku termičku provodljivost, koriste se za prenos apsorbovane energiju sa površine do medija (tečnosti) koji se pri tome zagreva.

Za visoki koeficijent efikasnosti solarnih termalnih kolektora, najvažniji faktori su: 1) spektralno selektivna prevlaka, koja je sastavljena od ostrvca metala utisnutih u trodimenzionalnu matricu dielektrikuma sa solarnim absorbancom od $\alpha > 0.95$ i emisivnošću od $\varepsilon \leq 0.05$. Obično, takve su prevlake na bazi TiN_xO_y dobijene fizčkom depozicijom iz gasne faze (PVD proces), kombinacijom magnetronskog rasprašivanja i depozicije katodnim lučnim rasprašivanjem i poboljšanim konstrukcionim rešenjima solarnog toplotnog prenosa sa površine apsorbera do medijuma, koristeći pri tome različite dizajne apsorbera.

U tom kontekstu, solarne selektivne prevlake su veoma važan deo površine apsorbera. One imaju prednosti u odnosu na prevlake dobijene galvanizacijom ili rasprašivanjem, koje se tradicionalno koriste u solarnim aplikacijama. Njihov pravilan dizajn i optimizacija slojeva omogućava dobijanje višeslojnih prevlaka, strogo kontrolisane debljine u svakom sloju, što je posebno važno. Naime, transformacija solarne iradijance za zagrevanje i prenos toplote iz prevlake na podlogu materijala kao što su: Cu, Al, nerđajući čelik, staklo ili polimeri je veoma važan i razlikuje se od podloge do podloge. Obično, ovakve prevlake poseduju debljinu od svega nekoliko stotina nanometara, pri čemu svaki sloj ima specifičnu funkcionalne ulogu u samoj prevlaci. Generalno sastav prevlake čine: zaštitni sloj, antirefleksivni sloj, nekoliko slojeva apsorbera, najčešće na bazi kermeta, difuzioni sloj i infra crveni reflektivni sloj.

Glavni fokus u ovom radu je na optičkim osobinama nanoprevlaka dobijenih primenom PVD postupka, koji omogućava dobijanje visoko selektivnih prevlaka sa maksimalnom absorbcijom, minimalnom emisivnosti i visokom efikasnosti solarnih termalnih kolektora, čiji je ključni funkcionalni element apsorber obložen sa selektivnim prevlakama.

Ključne reči: Nanoprevlake, termalni kolektori, solarna energija, dizajn.

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