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COATING MATERIALS FOR SPECTRALLY SELECTIVE SOLAR ABSORBERS: A BRIEF REVIEW

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Abstract: The use of energy from solar sources is a necessity, since by reducing fuel consumption from non-renewable sources we support both the sustainable development concept and environmental protection by pollution reducing. It is known that gas or wood-fired heater used in most homes eliminate air pollutant gases. Thereby anyone can use the free energy that the sun offers us, using solar thermal collectors, as an additional system, to prepare domestic hot water or for houses heating. There are several types of solar collectors, but all of them have a common key component called the absorption plate, or solar absorber, that captures as much energy as possible from the sun and transforms it into heat. But in order to obtain good results in terms of photo-thermal efficiency, the selective solar absorption plate must have an absorption coefficient (α) as close as possible to the value of 1 in the solar spectrum range of 0.3–2.5 μm and a thermal emittance coefficient that tends towards 0 for wavelengths greater than 2.5 μm (infrared range). For this purpose, the researchers studied the influence of different types of coatings deposited on the absorption plate substrate, on the photo-thermal conversion efficiency. For evacuated tube collectors, evacuated flat plate solar collectors and concentrate solar power unit, the coating must maintain its properties at medium and high temperatures. In this article is reviewed the progress made in recent years by researchers regarding the coating materials used for spectrally selective solar absorbers in terms of photo-thermal efficiency.

Keywords: solar energy, spectral selectivity, absorber plate, absorptance, emittance

INTRODUCTION

Obviously, the use of energy from solar sources is a necessity, so it has already become a significant component of the energy used worldwide.

Like a giant continuous fusion reactor [1] the sun, emits energy in the form of radiation. Therefore, this renewable, inexhaustible, clean and free source of energy it's used more and more nowadays to generate electricity or to heat water or air. The most significant fusion reaction produced in the interior of the solar sphere is a process in which 4 protons of hydrogen combines to form one helium nucleus, with energy generation and a loss of mass [1]. The reaction is accompanied by an emission of electromagnetic radiation with a very large wavelength range. Though, 99% has a wavelength in the range of 0.15 – 4 μm [2]. The main components of solar radiation reaching the Earth in different percentage are: ultraviolet radiation ($\lambda < 0.38 \mu\text{m}$), visible radiation ($\lambda = 0.38 \div 0.78 \mu\text{m}$) and infrared radiation ($\lambda > 0.78 \mu\text{m}$) [1]. The solar thermal collectors can capture a part of this radiation and transform it into thermal energy, so necessary in domestic, industrial or agricultural uses. For example, flat-plate solar collectors, works at temperatures under 100 $^{\circ}\text{C}$, while the concentrated solar power unit

function at mid (100 $^{\circ}\text{C} < T < 400 ^{\circ}\text{C}$) or high temperature ($> 400 ^{\circ}\text{C}$) [3]. Another two collectors category widely used that operate at medium temperatures ($< 200 ^{\circ}\text{C}$) are the evacuated tube collectors and the evacuated flat plate solar collectors. Both are low cost, can produce heat for low and medium temperature application [4] but the last one seems to be a more efficient option [5].

Flat-plate solar collectors have the interception and absorbing area equal (Figure 1a). The main components and operation mode are described more detailed in reference [6].

Evacuated flat plate solar collectors, as can be seen in Figure 1b, have a similar construction to flat-plate collectors, but the inner space has moderate vacuum, or contain a low-pressure gas like krypton or xenon instead of air [5]. The evacuated tube collectors, operated based on the heat pipe principle, and includes a specific number of vacuum tubes depending on the manufacturer. Each of them contains the absorber plate coated with a highly selective film (Figure 1c), which ensures an efficient capture of solar radiation and reduced losses through thermal radiation [7].

Regardless the solar collector type, one of the most important part is the spectrally selective absorber plate. Usually, it consists of a metallic

substrate, on which one or more layers of different thicknesses are deposited, using different techniques. The material used as substrate must have a high conductivity, while the spectrally selective coating deposited on the substrate a high absorptance in order to transfer as much heat as possible to the working fluid. Regardless of the layers number deposited on the substrate, in this paper the first layer is considered at the coating top (the last applied) and last one is considered the one deposited on the substrate, so the first applied.

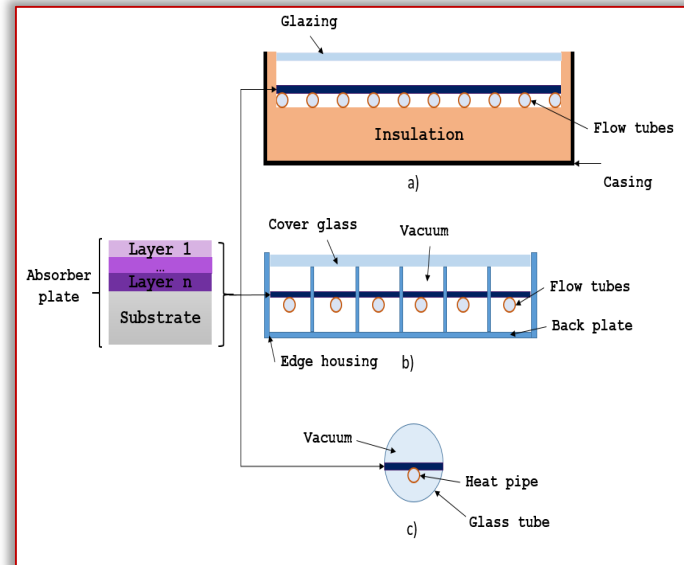


Figure 1. Simplified cross section of a solar thermal collector [reproduction from references [5,7,8]].

(a) Flat-plate solar collector. (b) Evacuated flat plate collector. (c) Evacuated tube collector.

The purpose of this paper is to give a general view onto the technical solutions applied to the construction of the solar selective absorber, in order to increase its photo-thermal conversion efficiency.

SPECTRAL SELECTIVITY

An opaque solid either absorbs or reflects the total incident radiant energy (per surface unit and per time unit). The ratio of energy absorbed by a solid and the total incident energy is named absorptivity (α), meanwhile the ratio of total energy emitted by the solid to that emitted by a perfect black body, both being on the same temperature, is named emissivity (ε) [9].

The coating of solar collector's absorber plate should have a high spectral selectivity evaluated by the two above mentioned coefficients note with (α_s) and (ε).

The solar absorptivity α_s can be calculated by Eqs. (1) [10]:

$$\alpha_s = \frac{\int_{\lambda_1}^{\lambda_2} (1-R(\lambda))I(\lambda)d\lambda}{\int_{\lambda_1}^{\lambda_2} I(\lambda)d\lambda} \quad (1)$$

where: $\lambda_1 - \lambda_2$ is the integral wavelength intervals, $R(\lambda)$ is the spectral reflectance of the coating and $I(\lambda)$ is the solar spectral irradiance. The thermal emissivity ε can be calculated by Eqs. (2) [10]:

$$\varepsilon = \frac{\int_{\lambda_1}^{\lambda_2} (1-R(\lambda))E_{b\lambda}d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{b\lambda}d\lambda} \quad (2)$$

where $E_{b\lambda}$ is the blackbody radiation.

According to Ning Y. et al. the photo-thermal conversion efficiency at working temperature, can be calculated by Eqs. (3) [11]:

$$\eta = \alpha_s - \frac{\varepsilon_T \sigma T^4}{CI} \quad (3)$$

where: η is the photo-thermal conversion efficiency, σ is the Stefan-Boltzmann constant ($5.67 \times 10^{-8} \text{ W/m}^2\text{K}^4$), T is the working temperature, C is the concentration factor and I solar radiation (W/m^2) [11,12].

The thermal emissivity ε_T at a definite temperature T can be calculated by Eqs. (4) [13]:

$$\varepsilon_T = \frac{\int_{\lambda_1}^{\lambda_2} (1-R(\lambda,T))E_{b\lambda}(\lambda,T)d\lambda}{\sigma T^4} \quad (4)$$

where: $E_{b\lambda}(\lambda,T)$ is the blackbody spectral irradiance at λ and T .

PHOTO-THERMAL CONVERSION EFFICIENCY

Absorber plates, the solar collector's active elements, are generally made of highly conducting metals as substrate [14] coated with solar selective materials that absorb the incident solar radiation (sunlight) and transform it into heat. The coefficients that characterize these phenomena are the thermal emittance and solar absorptance of the respective coated surfaces. In order to obtain a high photo-thermal conversion efficiency, the solar collector's selective absorbers should have high solar absorptance, close to the maximum value of 1, and a low thermal emittance ($\varepsilon \rightarrow 0$) coefficients [12,15,16]. The solar absorptance (α_s) must be high in the wavelength range of $0.3-2.5\mu\text{m}$, while the thermal emittance must be low in the infrared (IR) region above $2.5\mu\text{m}$ [10]. Materials with such properties ensure reduced losses through thermal radiation. In his studies Bello et al. [10] mentions that an appropriate

spectral selectivity cannot be obtained by using a single material.

Another important factor that influences the photo-thermal performance is the incidence angle of light imposed on the spectrally selective solar absorber plate coating (0–50° for non-concentrated flat plate solar collectors). According to Kumar K.K. et al. a coating surface with a wide angular solar absorptance improves the collector performance [17]. In general solar absorptance decreases with the incidence angle as can be noticed on references [12] (from $\alpha_s=0.976$ to $\alpha_s=0.957$ for an incidence angle of light of 50°), [17] (from $\alpha_s=0.94$ to $\alpha_s=0.89$ for an incidence angle of light of 50°) and [18] ($\alpha_s = \text{near } 1$ for an incidence angle of light $\theta < 65^\circ$).

The conversion rate it also depend on the type of absorption plate, the materials used in its construction and, of course, a number of factors such as those related to the layers preparation techniques, as can be deduced from the specialized literature. Al-Rabeeh A.Y. et al. [19] specified that there are five types of solar selective absorber coatings (SSACs) able to achieve high photo-thermal efficiency namely: cermet, multilayer (dielectric-metal-dielectric) stacks, semiconductor, intrinsic and textured surfaces.

In an attempt to reach an optimal spectral selectivity, one or more layers obtained from different materials or a combination of them, with suitable thickness and properties and an interesting and unexpected configuration, were deposited on a substrate through different methods, some simpler, others more complex.

Generally, the absorption plate substrate can be made of stainless steel, copper, aluminum, Inconel 625 (nickel-base alloy), and the transmission of heat stored to the thermal agent is his main purpose.

By techniques as sputtering [3,10,12,13], anodization (electro-chemical deposition) [16], dip-coating followed by annealing [17], spraying [20], etc., the layers are deposited on the substrate. For example, in Figure 2 is shown a simplified structure of cermet (metal-dielectric) double layer composite absorber plate. The cermet layers (layer 2 and 3) consist of fine metallic particles incorporated in a dielectric host matrix [3,15]. The upper one contain a low metal volume fraction (LMVF), while the lower a high metal volume fraction (HMVF). The layer deposited on the substrate (IR reflector) is necessary to reduce losses through radiation, while the first one (AR coating) is an

antireflection layer which reduces the phenomenon of solar reflection on the absorber plate surface [15].

Nuru Z.Y. et al. [3] specified in their studies that in order to achieve a low thermal emittance of the solar absorber an IR reflecting layer should be deposited on the substrate that reflect low in the visible and high in the infrared region (given that the substrate will emit thermal radiation with wavelengths in the IR range). The most used metals with high reflectance, deposited by different methods are: Mo (97% reflectivity in NIR spectral domain [3]), Al (88% reflectivity [19]), Ag (98% [19]), Ni, Au and W.

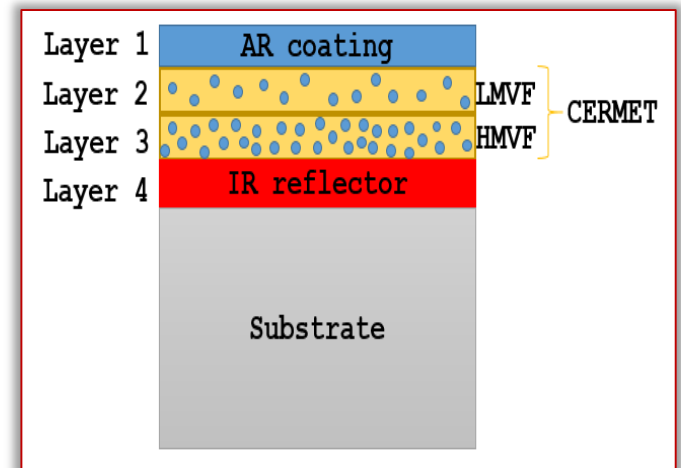


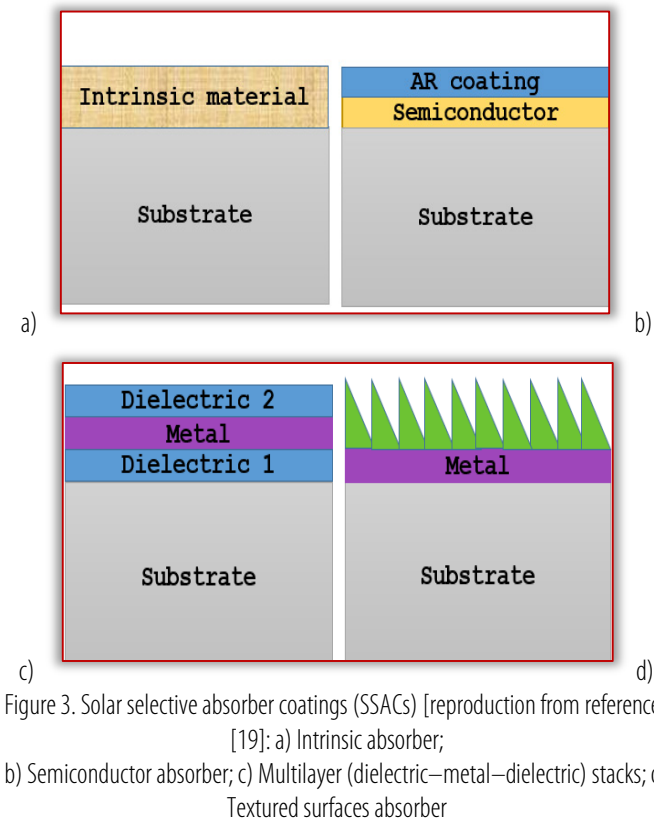
Figure 2. Cermet double layer composite absorber structure [reproduction from references [12]]

This type of structure is a complex one, but there are a lots of film configuration types and number of layer deposited on the substrate mainly for multilayer solar coatings.

According to the studied literature, it seems like five layer are the maximum number deposited on the substrate. Also we find that the layer thicknesses deposited varies from a minimum of 9.1–9.5nm Al_2O_3 film deposited by anodization [16] to a maximum of 110 nm $\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{0.89}$ [21]. An oxidized stainless steel substrate can have a thickness of about $2\mu\text{m}$ (2000nm) [22], a sprayable polymer (PEDOT:PSS) applied on a substrate can reach up to 5800 nm [20], meanwhile a nanocomposite film can have a thickness of 300nm [23].

As mentioned, beside cermet SSACs presented in Figure 2 there are another four type of simplified structure illustrated in Figure 3.

The intrinsic absorbers (figure 3.a) are obtained by depositing on a substrate of an intrinsic material layer that has inherent spectral selectivity [24]. That layer usually contain transition metals or semiconductors [19] whose properties are enhanced by doping, for example.



Semiconductor absorbers (figure 3.b) are formed from a semiconductor layer over which it is applied an antireflection coating. The semiconductor layer uses bandgap properties to absorb short – wavelength radiation [14].

Dielectric–metal–dielectric stacks, known as multilayer absorbers (figure 3.c), efficiently absorb the solar radiation due to the phenomena of multiple reflection [25], while textured surfaces absorber (figure 3.d) are characterized by multiple reflection and absorption effects that rise the collector photo-thermal efficiency.

There have been efforts to optimize both the substrate materials as well as the coating of the solar absorber in order to increase the conversion efficiency of solar energy into thermal energy, as we can see in Table 1.

As can be seen from table 1, in the compenence of studied solar absorber layer structures appear very often alumina (Al_2O_3). This layer either has the role of an antireflection layer named AR coating, or is part of the absorption layers as: dielectric host matrix in cermet layers, pigmented porous layer or intrinsic layer.

According to Niranjana K. et al [26], a perfect spectrally selective coating must meet the following requirements: thermal stability at high temperatures, a solar absorptance coefficient higher than 0.95 and a thermal emittance coefficient lower than 0.10.

Table 1. Spectrally–selective coatings

Solar absorber layers structure Layer 1(Upper layer)/Layer 2/... Layer n (lower layer–deposited on the substrate)	Substrate	Preparation	Solar absorptance (α_s)	Thermal emittance (ϵ)	Ref
MgF_2 (AR coating)/NiCr– MgF_2 (LMVF)/NiCr– MgF_2 (HMVF)/Au(IR reflector)	stainless steel	Sputtering	0.976	0.045 at 25C	[12]
Al_2O_3 (AR coating)/Pt– Al_2O_3 (LMVF)/Pt– Al_2O_3 (HMVF)/Mo(IR reflector)	stainless steel/glass	Sputtering	0.97	0.05 at 80C	[3]
Ti/AlN/Ti	Fe_2O_3 decorated SS 316L	Sputtering	0.896	0.190	[10]
AlN/Ti/AlN/Ti/AlN	Fe_2O_3 decorated SS 316L	Sputtering	0.82	0.27	[10]
Sn– Al_2O_3 (Sn pigment deposited into the pores of Al_2O_3)	Aluminum	Anodization and electrolysis	0.94	0.21 at 100C	[16]
Co– Al_2O_3 (Co nanocylinders embedded in the pores of Al_2O_3)	Aluminum	Two step electrochemical anodization	above 0.98 (for 200–1100nm spectral range)	0.03 at 100C	[25]
Al_2O_3 /Al(IR reflector)	stainless steel SS304L	Sputtering	0.916	0.05	[13]
Al_2O_3 /Ni(IR reflector)	stainless steel SS304L	Sputtering	0.913	0.15	[13]
SiO_2 /Cr $_3\text{O}_3$ /Cr/Cr $_3\text{O}_3$ /Cr / Cu	glass	E–beam vapor deposition and sputtering	0.97	0.05 up to 300C	[4]
(SiON/SiO)(AR coating)/WAlSiN/W $_{1.6}$ N interlayer/W(IR reflector)	stainless steel	Sputtering	0.94	0.16 at 800C in vacuum	[26]
Al_2O_3 (AR coating) /ZrB $_2$ / TiC–ZrB $_2$	stainless steel	Sputtering and annealing in vacuum	0.92	0.10 at 82C	[27]
Al_2O_3 /Cr $_{0.53}\text{Al}_{0.47}\text{N}_{1.12}$ /Cr $_{0.96}\text{Al}_{0.04}\text{N}_{1.08}$ /Cr $_{0.95}\text{Al}$	316L steel	Sputtering	0.96	0.14 at 25C	[21]
Al_2O_3 /Cr $_{0.53}\text{Al}_{0.47}\text{N}_{1.12}$ /Cr $_{0.62}\text{Al}_{0.38}\text{N}_{1.00}$ /Cr $_{0.96}\text{Al}_{0.04}\text{N}_{0.89}$	316L steel	Sputtering	0.96	0.15 at 25C	[21]
Thin nanocomposite film (Co $_3\text{O}_4$:Cr $_2\text{O}_3$ /C)	Aluminum/ glass	Spin coating and casting methods	0.88–0.932 (for 250–1300 nm spectral range)		[23]
MgF_2 (AR coating) /Nanocomposite absorber (SiO $_2$ nanoparticles)	stainless steel SS304	Dip–coating and annealing at 500C for 1h	0.94	0.14	[17]

Nanocomposite absorber (0.5 wt% SiO ₂ nanoparticles)	stainless steel SS304	Dip-coating and annealing at 500C for 1h	0.92	0.12	[17]
W(square ring)/Al ₂ O ₃ /W/Al ₂ O ₃ /W	sapphire	Electron beam evaporator and electron beam lithography	max. 0.9626 (for 280–2280 nm spectral range)		[28]
Polymer (PEDOT:PSS)	stainless steel	Spray technique	0.967	0.36 at 82C	[20]
Al ₂ O ₃ (AR coating)/NiCrAlO/Au(IR reflector)	stainless steel	Sputtering and water boiling	0.964	0.066 at 25C	[29]
CuMnO/CuO (with a fractal structure)	Inconel 625	Electrodeposition	0.985 (for 350–1100 nm spectral range)	0.41	[18]
Oxidized surface (Cr ₂ O ₃ //Fe _{3-x} Cr _x O ₄ /Fe ₂ O ₃ //diffusion zone)	stainless steel SS304	Isothermal annealing at 900C for 8.76h	0.92	0.37	[22]
SiO ₂ /SiON/Ti(B,N)/TiB ₂	stainless steel SS304	Pulsed direct current (DC) and radio frequency (RF) magnetron sputtering	0.981	0.15 at 82C	[30]
SiO ₂ /Ni _x Co _{3-x} O ₄ ; 0≤x≤1	stainless steel SS304	Wet-chemical dip-coating	0.94	0.13	[31]
SiO ₂ (AR layer)/AlN(AR layer)/TiAlN/AlN/Pt(IR reflector)	Austenitic stainless steel	DC magnetron sputtering	0.92	0.04 at 82C	[32]
MgF ₂ /Al ₂ O ₃ /TiO ₂ /Ti/SiO ₂	Fe	Physical Vapor deposition	0.943	0.28	[33]
SiO ₂ /Co-Cr	stainless steel SS304	Electroplating and dip coating	0.96	0.12	[34]

Various types of spectrally selective coatings have been studied, obtained simply (e.g. by spraying) or through more complex techniques, some used in other fields that seem to find applicability for the study in question, such as polymers. For example, Selvakumar et al. [20] prepared a polymer based spectrally selective coating that, for the optimized thickness of the layer (5.8μm) reported an absorptance of 0.967 and an emittance of 0.36. It seems that materials based on polymers are being researched in recent years as a potential low-cost coating materials for solar absorber coatings. Another cost-effective technique studied by P. Ranganathan et al. [22] is thermal oxidation by air annealing of the absorber plate substrate made from stainless steel (SS304). A new complex type of fractal-textured coating was studied by Kant K. et al. [18] who

obtained through electrodeposition followed by annealing at 500°C a fractal structure at the upper layer which shows an exceptional solar selectivity. They discovered that the surface roughness of the multiscale textured surface increases by increasing the fractal dimension (which has multiple internal reflection surfaces) and so intensify light trapping in between the asperities thus enhancing the solar energy absorption.

D. Kharkhan et al. demonstrated with good results that thermochromic LaCoO₃ selective layer used in the construction of SSACs has the capacity of changing the IR emissivity at stagnation temperatures in order to evite self-heating of the thermal solar collector [35].

Regarding the configuration of solar collector absorption plates, in recent years a number of interesting models have been investigated in terms of the geometric configuration of the upper surface. For example B. B. Han and co-authors designed and studied a structure made up of three layers of different materials: (Si, TiC, Graphene) over which another structure was deposited whose basic cell consists of two ring-type Titanium semicircles placed back to back and intersected on a portion (Figure 4.a). The results showed that the efficiency is greater than 97% for a wavelength of 600nm [36].

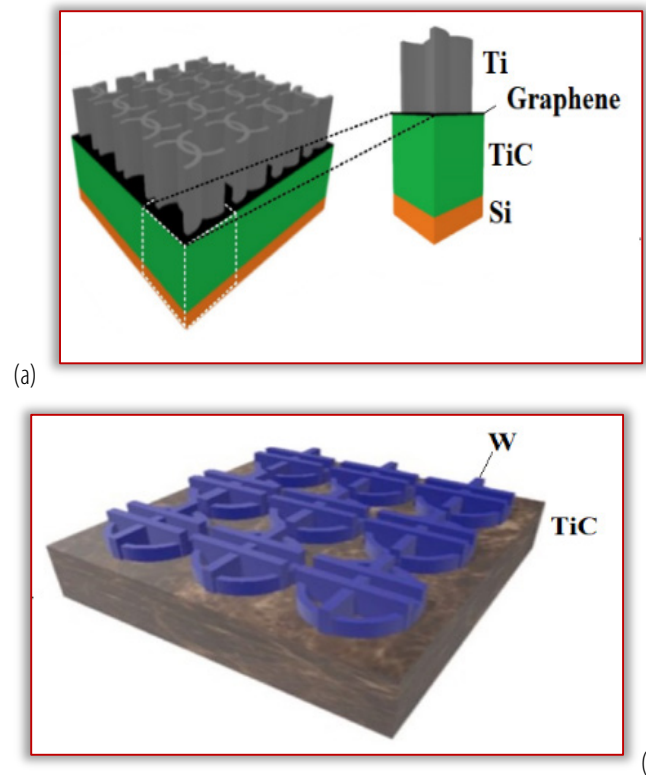


Figure 4 – D SSACs structure configuration: a) [36]; b) BRBSA [37]

The absorber plate created by H. Patel and co-authors is named Block Ring Base Solar Absorber (BRBSA) and is formed by the

dielectric base layer (TiC) over which the tungsten resonator is applied, which has the shape of figure 4.b. The highest efficiency of 97.89% was obtained in the visible region [37]. B. Qi et al. designed a Dual-dielectric-layer metamaterial selective absorber (DDMSA) consisting of 4 layers (W and Al_2O_3 alternating layers), and on top of that a W square structure was deposited, the shape of which can be seen in figure 5. [28].

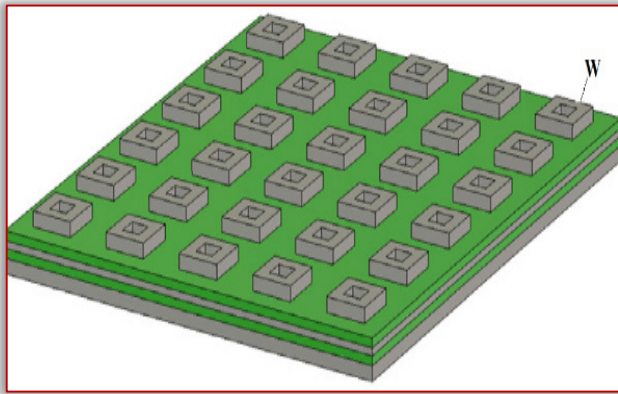


Figure 5 – D SSACs structure configuration [28]

According to the literature studied, it can be concluded that in this field research is intense and focused on obtaining optimal absorbance and emissivity coefficients for the absorption plates of solar collectors. Researchers in the field are trying new materials, new surface geometries and of course are focused on obtaining optimal spectral selectivity, at reasonable prices.

CONCLUSIONS

The sun, indispensable to life, offers us an inexhaustible, free and clean source of energy that can be used in many fields, but also can be captured by thermal solar collectors.

From the literature studied, the following is concluded:

- The absorbance and emissivity of the SSACs (solar selective absorber coatings) varies depending on: the type of absorption plate, the material of the substrate, the number and thickness of the layers, the absorber plate design, the properties of the chemical elements and the chemical compounds used, the percentage amount used, the deposition technics, etc.;
- The most appropriate metals deposited on the substrate and used as IR reflectors, with a thermal emittance below 0.1, are: Au, Mo, Al and Cu;
- SiO_2 (most used), Al_2O_3 and MgF_2 are the most predominate materials used as antireflection layers;

- Materials such as polymers applied by spraying onto the substrate, or subjecting the substrate itself, which is mainly made of stainless steel to heat treatments, reduce the production cost of solar collectors and can be cost-effective;
- Different geometric configurations of the SSACs upper layer has been investigated, with promising results.

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