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Editorial

Spectrally Solar Selective Coatings in Absorbing Layers: Theoretical Investigation Using MATLAB

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Abstract

Background: In order to describe the spectral reflectivity of the multilayered selective coating, a theoretical investigation of the optical properties was settled. **Materials and Methods:** Since the reflectance spectrum involve the matrix operation, hence in this theoretical investigation MATLAB® is utilized to investigate and foresee nanostructured solar selective coatings in solar thermal collectors. The nanostructured pure layer such as Au, Ni, Cr and Ag utilized and sandwiched aluminium nitride (AlN) solar selective coating. A demonstrative solar absorber has been studied regarding optical characterization and calculation improvements. It can be seen that copper has good ultraviolet (UV), moisture and environmental steadiness for c.a. 600 h in air up to c.a. 230-250°C. While Ni, Cr and Ag coating have been cited in the literature for high-temperature applications and they possess better stability. Additionally, two different grades of stainless-steel namely one austenitic (832 MV) and one ferritic (393 M) has been examined. **Results:** The austenitic steels have a higher absorptance than the ferritic steels and other utilized metals. Another challenge was measuring the efficiency of solar thermal energy conversion systems; it was found that Ferritic-SS has the best photothermal conversion efficiency among the examined metals. **Conclusion:** The theoretical results found in this study, in general, were in respectable agreement with the experimental results.

Key words: Solar absorber, nano-structures, MATLAB, spectrally selective surface, reflectance and emittance

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

In general, solar selective coatings absorb solar radiation and convert it into thermal energy. Spectrally selective surfaces for solar absorbers have been investigated since the 1950s, when the idea of utilizing wavelength discrimination and wave front discrimination was introduced. Capable usage of the sun's power, either with a flat-plate or a focused type of collector system, involves a capable solar-absorbing selective coating. Solar thermal systems are rapidly spreading into various application areas. In numerous countries people started to build plane plate solar collectors for domestic hot water and house warming^{1,2}.

Most solar collectors utilize a spectrally selective absorber surface which has high absorptance, at solar spectrum range and low emittance, at infrared spectrum range to minimize heat radiation failure. Additionally, absorptance is a degree of the aptitude of an object to absorb solar radiation, while emittance is the competence of a surface to radiate energy. Considerable investigation and development was conducted during the later half of the 1970s and the early 1980s on coatings and surface treatments yielding such properties, i.e., high absorptance and low emittance³.

Solar selective coatings are the most significant part of solar collectors, which straightforwardly, affect the efficiency of the solar-to-thermal energy modification. A selective solar absorber must possess high solar absorptance in the solar energy spectrum (0.3-2.5 μm) so as to capture maximum solar energy and low emittance in the infrared region (2.5-20 μm) to moderate energy losses⁴.

Moreover, the optical and physical properties of the coated surface must stay stable under long-lasting operation at raised temperatures, recurring thermal cycling, air exposure, ultraviolet radiation, etc and similarly the adherence of the coating to the substrate must be suitable. From a real-world viewpoint, the method of coating should be simple and economic.

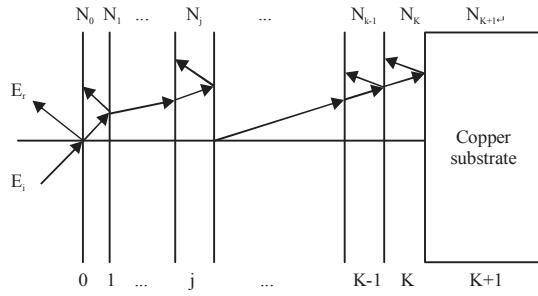
Currently, black nickel, black chrome and black copper appear as the most capable and achievable selective coatings^{5,6}. Black deposits containing chromium are utilized as commercial appearances under the name "Black chrome". Black chrome is commonly utilized in solar collectors because of its high absorptance, proper stability and high thermal resistance. Conventionally, the solar selective coatings are electro deposited on metallic substrates, such as Ni, Cu and steel from a hexavalent chrome bath by means of pulse current electrolysis to increase the optical aspects of the coatings⁷.

Preliminary solar selective coatings designed for usage in global systems were applied to plane plate collectors. More recent study demonstrated that solar selective coatings could be applied to glass tubes at the focus of trough style collectors⁸. Sputter deposition was initially utilized to produce the molecular combinations of metal and dielectric on the outward of the glass tubes. A tungsten and aluminum nitride combination was found to be an operative candidate. Further work on solar selective coatings for space power applications utilized ion beam sputter deposition, where the molecular mixtures of metal and dielectric were made with a modified cylindrical target⁹. Numerous of these coatings were considered for their stability in atomic oxygen and vacuum ultraviolet environments¹⁰. Coating thickness and chemical composition were also treated as variables in optical characterization. A wide-ranging review on medium to high temperature solar selective absorber materials are well-described independently by Kennedy¹¹ and Ho and Iverson¹².

MATERIALS AND METHODS

In this study, we theoretically examine the nanostructured aluminum nitride-metal-aluminum nitride (AlN-M-AlN) solar selective coating. Besides, a characteristic solar absorber has been investigated in terms of optical characterization and scheming optimization. The MATLAB® is an arithmetical computing tool was utilized to do the measurements of multilayer solar selective coatings. The MATLAB® permits the matrix operation and yields the required graphs. Reliant upon the matrix method, the reflectance spectrum can be achieved. At that moment, the absorptance and the emittance are assessed from the reflectance spectra by amalgamation of the solar radiation spectrum. This method has been utilized for the optical measurements on the multilayer coatings and the optimization of the structures of the AlN-M-AlN solar selective coating.

The optical representation of multilayer absorbers is characterized by interference effects of reflected light between various interfaces and the incident light. The characteristic pattern of multilayer absorber is assumed¹³ in the Fig. 1. Moreover, the multilayer absorbers possess high solar absorption, i.e., low thermal emittance, which can be enhanced by computer modeling¹⁴. Generally, thicker AlN-M-AlN solar selective coatings possess higher thermal emittance. Thus, the AlN-M-AlN combination coating is typically nanostructured and the overall thickness should be less than 1 μm .



$$r = \frac{N_0 - B/E}{N_0 + B/E} \quad (4)$$

Also, the reflectance of the system of K layers can be calculated as Eq. 5:

$$R = \left(\frac{N_0 - B/E}{N_0 + B/E} \right) \left(\frac{N_0 - B/E}{N_0 + B/E} \right)^* \quad (5)$$

Fig. 1: A multilayer stack scheme of K layers on a metallic substrate⁶

It has recognized that the reflection of light from a single interface can be characterized by the Fresnel equations. Nevertheless, for multiple interfaces, presented in Fig. 1, matrix method is utilized to compute the reflection coefficient.

To enhance the AlN-M-AIN solar selective coating, the multilayer coatings were simulated by using MATLAB[®]. The MATLAB[®] packages of multi-layer coatings facilities the matrix mode to compute the reflectance. Explicitly, after supposing that the light has vertical incidence, the system of K layers is considered by the feature matrix:

$$\begin{bmatrix} E \\ B \end{bmatrix} = \prod_{j=1}^k \begin{bmatrix} \cos\delta_j & \frac{i}{N_j} \sin\delta_j \\ iN_j \sin\delta_j & \cos\delta_j \end{bmatrix} \begin{bmatrix} 1 \\ N_{k+1} \end{bmatrix} \quad (1)$$

where, E and B are total electric and magnetic field amplitudes of the light propagating in the medium. Additionally, $i^2 = -1$, N_j is the refractive index of the jth layer and δ_j is the phase thickness of the jth layer.

The typical matrix at a wavelength λ for the association of N layers is given by Eq. 2:

$$M = M_1 M_2 \dots M_n \quad (2)$$

Therefore, each layer is characterized by a 2×2 matrix M_j of the arrangement:

$$M_j = \begin{bmatrix} \cos\delta_j & \frac{i}{N_j} \sin\delta_j \\ iN_j \sin\delta_j & \cos\delta_j \end{bmatrix} \quad (3)$$

where, $\delta_j = 2\pi n d_j / \lambda$ with the physical thickness of the layer being d_j , then the reflection coefficient r and the reflectance R are correspondingly assumed using:

In which, the refractive index, $N_0 = 1$ for air. For multilayer coatings, the absorptance and emittance can be measured by associating the reflectance spectra with the solar spectra. Moreover, for a compound layer, for instance SS-AIN layer, effective medium theory (Brugge man model) is utilized. The optical constants of compositions can be found¹⁵. The Brugge man's approximation for spherical particles in an effective medium is conferred in the coming Eq. 6:

$$f_M \frac{\epsilon_M - \epsilon^{ER}}{\epsilon_M + 2\epsilon^{ER}} + (1 - f_M) \frac{\epsilon_D - \epsilon^{ER}}{\epsilon_D + 2\epsilon^{ER}} = 0 \quad (6)$$

where, f_m is the volume fraction of metallic component, ϵ is dielectric functions, indexed by M for the metal, D is the dielectric component respectively and ϵ^{ER} is dielectric function of metal-dielectric composite attained from Brugge man model.

If the dielectric constant of medium and metal spherical particle is ϵ_1 and ϵ_2 respectively, dielectric constant of two-phase amalgamated system ϵ can utilize the following Eq. 7:

$$\epsilon_M = \epsilon_1 \frac{\epsilon_2 + 2\epsilon_1 + 2f_M(\epsilon_2 - \epsilon_1)}{\epsilon_2 + 2\epsilon_1 - 2f_M(\epsilon_2 - \epsilon_1)} \quad (7)$$

The relationship between complex refractive index, N , of composite system at optical frequency and effective complex dielectric constant ϵ is presented in the following Eq. 8:

$$N = n + ik = \sqrt{\epsilon} \quad (8)$$

where, n and k are the refraction rate of composite system and coefficient of extinction in that order.

It is important to improve the efficiency of solar thermal energy conversion systems which will intensely reliant upon the optical characteristics of solar selective materials and construction. Therefore, the function η is utilized to define the photo thermal conversion efficiency of selective coating including absorptance (α) and emittance (ϵ) as following Eq. 9:

$$\eta = \alpha \times (1 - \epsilon) \quad (9)$$

Moreover, solar spectrally selective absorbers should possess the feature to enhance the solar energy absorption by trapping the photons in the structures and simultaneously minimize the defeat of thermal radiation emission¹⁶. Preferably, these materials should perform as a perfect photon absorber over a wide-ranging solar spectral region and a perfect reflector in the thermal infrared (IR) region.

RESULTS AND DISCUSSION

Usually, a black object is made from a material that absorbs all received light. Although in real world objects which look black reflect constantly some light and accordingly the ideal black object does not exist. There is not any material that absorbs 100% of light at all angles and over all wavelengths. Therefore, materials utilized as solar panel should be efficient of absorbing, storing and transmitting energy from the sun to a transport medium with minimum thermal losses. Accordingly, for this application, one must maximize absorption ($\alpha > 0.95$) and minimize emittance ($\epsilon < 0.10$) of the utilized materials. Additionally as transmission is typically by conduction, a satisfying thermal conductivity is required¹⁷.

Figure 2 is a cross-sectional representation of two selective composite coatings one with particles homogeneously distributed in the matrix, sandwiched between two AlN layers and the other with classified index micro structure which is Cu in this case. Noticeably, copper has good ultraviolet (UV), moisture and environmental stability for c.a. 600 h in air up to c.a. 230-250 °C. To protect the coating from degeneration, the surface can be coated with mechanically and chemically steady SiO₂ using the spray pyrolysis technique¹⁸. A double antireflection layer is employed, which is made up of a SiO₂ layer and an AlN layer. SiO₂ which is not given in Fig. 1, with the top AlN reduces the refractive index mismatch between air and the absorbing layer. The frontal surface reflection as a result of the SiO₂ coating was found to be thermally and chemically stable⁹.

The metal films are deposited on 1.1 mm thick soda lime silica glass (SLSG), which is utilized as a bottom layer in Fig. 2 is transparent for the solar spectrum. However, SLSG is opaque for the infrared wavelength and thus repress thermal radiation emitted from the absorber. Besides as glass reflects some of the incident solar radiation, therefore, an antireflection coating can be utilized with the aim of decreasing the reflection¹⁹. There are powerful absorption bands below 0.3 μm wavelength due to electronic transitions,

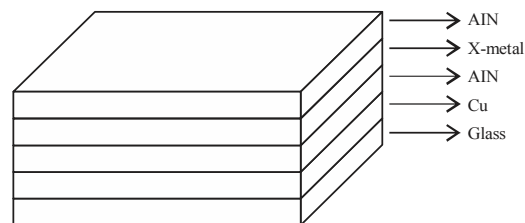


Fig. 2: Structure of the AlN-Metal-AlN solar absorber sample

especially in the Si-O bonds^{20,21}. These absorption bands do not effect solar applications, since hardly any sunlight penetrates the atmosphere below 0.3 μm wavelength.

The thickness of the three layers, AlN-Metal-AlN, where 30, 2 and 30 nm, respectively, such that the absorptance was maximized whereas the emittance is set aside approximately below 0.3. Divergent anti-reflection coatings is utilized, in an attempt to achieve an antireflection layer with a refractive index nearby the square root of the refractive index of the matrix in the visible region.

Solar selective coatings absorb solar radiation and change it into thermal energy. Since, black nickel, black chromium and black copper appear the most effective and practical selective coatings, therefore this investigation focused on these materials. For instance, electro deposited black nickel coatings have been widely discussed and revealed to possess good solar selective possessions. In addition, black nickel is most susceptible to humidity degradation^{22,23}.

Using MATLAB[®] the absorptance and emittance of the solar absorber was modeled utilizing the solar spectrum. The optical data i.e., refractive index and distinction coefficient, for Cu, Cr, Au, Ni and Ag were taken from Palik's book¹⁵. While, the optical data for two different types of stainless steel, one austenitic (832 MV) and one ferritic (393 M) were taken from Karlsson *et al.*²⁴. The spectra cover a wavelength range 0.3-8 μm, which is well-matched with the range of solar radiation spectrum. As the light diffuse scattering module is ignored for the bright and semi-bright black coatings, it is obvious that losses associated with the diffuse scattering module possess little influence on the values of spectral reflectance for the samples under study.

Black chromium is recognized to possess better corrosion resistance than nickel films mainly when formic acid is added to the electro deposition solution²⁵. From Fig. 3a and Table 1 a solar absorptance and a thermal emittance of 0.900 and 0.308, respectively were reported for AlN-Cr-AlN. This comparatively high absorption coefficient is because of the presences of Cr. Using Cr³⁺ instead of Cr⁶⁺ with an optimized design of the bath, similar results obtained by Bayati *et al.*²⁶

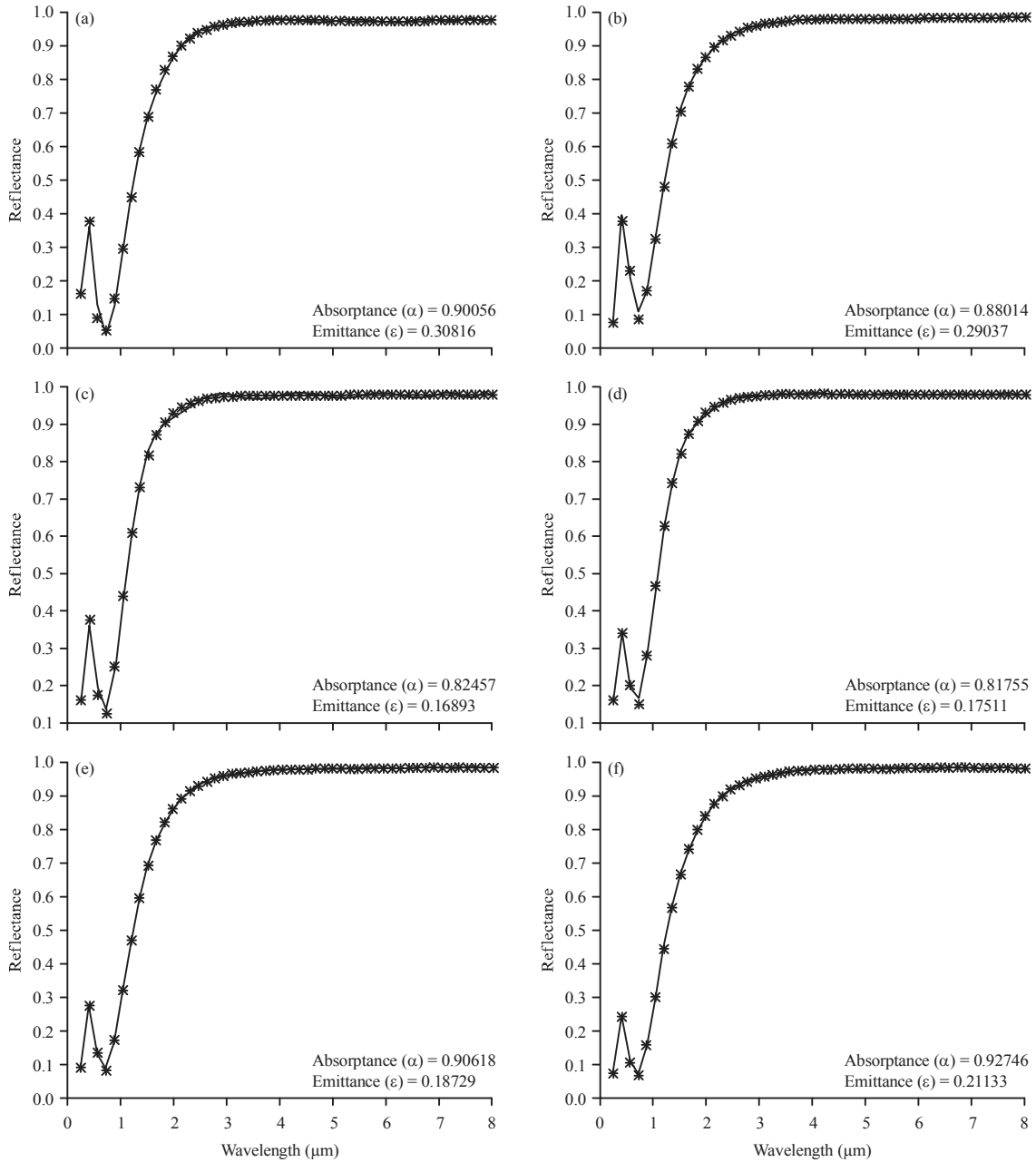


Fig. 3(a-f): Calculated reflectance spectrum versus wavelength of the (a) AlN-Cr-AlN, (b) AlN-Ni-AlN, (c) AlN-Au-AlN, (d) AlN-Ag-AlN, (e) AlN-Ferritic SS-AlN and (f) AlN-Austenitic SS-AlN solar absorber samples. Black lines represent the best fitting for the scattered points

Table 1: Absorbance and emittance of the selected materials coating

	Au	Ag	Cr	Ni	Austenitic-SS (832 MV)	Ferritic-SS (393 M)
Absorbance (α)	0.824	0.817	0.900	0.880	0.927	0.906
Emittance (ε)	0.168	0.175	0.308	0.290	0.211	0.187

and other co-researchers²⁷⁻³¹. The small inaccuracy is inevitable as a result of the control of manufacturing procedure and degradation of the coating.

Nevertheless, even though chromate is an exceptional corrosion inhibitor, it has been documented a highly toxic, sensitizing and cancer-causing. Meanwhile, Cr³⁺ is not toxic

and systematically looks a lot like the characteristics of Cr^{6+} it signifies the appropriate substitute for Cr^{6+} replacement³². In recent times, using ionic liquids, a formulation primarily rely upon on a Cr^{3+} plating solution was proposed to electro deposit black chromium³³.

It can be seen that from Fig. 3b and Table 1 AlN-Ni-AlN has absorbance value of the order of 0.880 and emittance value of the order of 0.290. However, Mehra and Sharma³⁴ reported that the black nickel film prepared on a zinc-coated electro polished aluminum possess absorbance value of the order of 0.90-0.94 and emittance ranging from 0.08-0.15. Undesirably, the obtained coatings by Mehra and Sharma³⁴ do not extant enough resistance to high moisture at higher temperatures. Therefore, this investigation is an effort to overcome this inconvenience using more stable black Ni coatings. On the other hand Lira-Cantu *et al.*³⁵ deposited black nickel on stainless steel by means of electrochemical deposition. Their coatings showed absorbance values between 0.91-0.96 and emittivity lower³⁵ than 0.1.

In contrast to Cr and Ni as indicated in Fig. 3c and d the emittance is decreased significantly when the metal replaced by Au and Ag, 0.168 and 0.175, respectively. While, the corresponded absorbance for Au and Ag were 0.824 and 0.817 in that order (Table 1).

Analogous manners of the optical constants are indicated in silver films^{36,37} and gold films^{38,39} that cover nano-voids with a size of a few nanometers. On the other hand, the refractive index n of thin films is a degree of the apparent phase alteration through the film, compared with the same distance in air. The electromagnetic energy gets conditionally trapped in plasmonic resonant conditions within the voids, producing delays in transmission and therefore, an increase in n ⁴⁰. Moreover, the extinction coefficient k governs the active reduction or skin-depth for light propagating over the film.

Finally as indicated in Fig. 3e and f two different grades of stainless-steel namely; one ferritic (393 M) and one austenitic (832 MV) has been examined in this study. Undesirably, only few studies have been recorded regarding these two types of steels⁴¹. It was found that, from these results, the austenitic steels have a higher reflectance than the ferritic steels. The lesser reflectance of the ferritic steels makes them desirable as principal metals in cycle collectors. Consequently, the corresponded absorbances for austenitic and ferritic steels were 0.927 and 0.906 in that order (Table 1). Noticeably, the corresponded emittances for austenitic and ferritic steels were 0.211 and 0.187 in that order (Table 1). A general observation from the primary absorbance data is that the reasonably large difference in composition among the samples has very slight influence on the absorbance. As an attempt to measure the

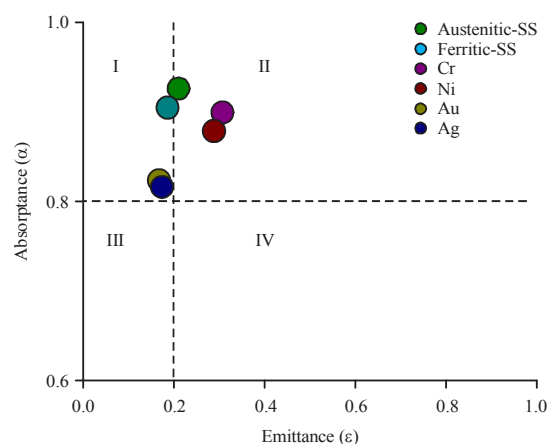


Fig. 4: Scatter graph of absorbance and emittance for representative AlN-M-AlN samples used in this study

optical constants for one austenitic and one ferritic grade, using the Kramers-Kronig analysis, Karlsson and Ribbing⁴² obtained relatively low absorbance and high emittance values.

These results specified that, utilizing these types of steels, i.e., austenitic and ferritic steels, there is significant improve in the particle growth and therefore the spectral selectivity of the optical properties. Consequently, it is vital to study the role of the optimization of the selecting materials so as to achieve the optimal optical properties.

Figure 4 shows a graph of absorbance versus emittance for samples utilized in this investigation showing how the absorbance and emittance combinations scattered. The quadrants were formed from a rule of thumb that good selective absorbers have to have a solar absorbance no less than 0.8 and a thermal emittance of less than 0.2. An effectual solar absorber should have absorbance values that are as close to 1 as possible whereas having emittance values as close to 0 as possible. Such absorbers drop into quadrant 1 of the graph shown in Fig. 4. Moreover, from Fig. 4 it can be agreed that the upper limit of solar absorbance for AlN-M-AlN in this study is 0.927 for Austenitic-SS (832 MV), however the lower limit is 0.817 for Ag. The upper limit of thermal emittance is 0.308 for Cr while the lower limit is 0.168 for Au. Therefore, using equation 9, the sample that had the best combination of absorbance and emittance was Ferritic-SS and thus it has the best photo thermal conversion efficiency with absorbance of 0.906 and a thermal emittance of 0.187 giving a photo thermal conversion efficiency of 0.736. Other photo thermal conversion efficiencies can be seen in Fig. 5. These optical properties compare well with the optimal SS-AlN sample of similar design as samples in this study fabricated by Zhang⁴³.

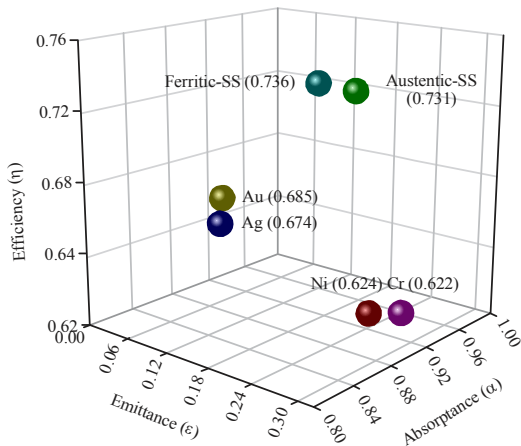


Fig. 5: A three-dimensional representation of photo thermal conversion efficiency as a function of emittance and absorptance for the materials used in this investigation

CONCLUSION

To achieve high solar absorptance, a thick coating is required but this gives high thermal emittance and does not fulfill the requirement of selective absorption. This investigation indicates that a selective thicknesses of the layers produce high solar-absorptance and at the same time relatively low thermal-emittance.

This investigation covers preparation and optical study of the absorbing surfaces utilized in solar thermal collectors. It also deals with coatings that can enhance the excellence of the absorbers. From our theoretical investigation, it was found that the AlN-Metal-AlN structure causes strong interference and this could not be achieved from the graded index layer structure of the M-AlN coating.

We conclude from these results that the austenitic steel would be the best for solar absorptance; the absorptance value around 0.927 is high as compared to Au, Ag and Ni. It is also concluded that emittance value of the austenitic steel is higher than the corresponded values of Au, Ag and ferritic steel. The results obtained in this investigation were compared with experimental results and a respectable agreement was found.

As the efficiency of solar thermal energy conversion systems depend on the optical characteristics of solar selective materials and structure. Therefore, this investigation showed that Ferritic-SS has the best photo thermal conversion efficiency i.e., 0.736, with absorptance of 0.906 and a thermal emittance of 0.187.

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