Abstract: A solar collector is an apparatus that collects the sunlight energy then alters this energy into a more usable or storable energy form. The absorber surface used in thermal solar collectors requires high absorptance in the solar spectrum and low emittance. Several techniques, such as vacuum techniques, are currently used to produce solar absorber surfaces. However, the desired characteristics of the solar absorber coating may be better controlled by direct electrodeposition such as their nanostructuration. Other electrodeposition advantages are basically rapidity, low cost, free from porosity and industrial applicability. Copper substrate was chosen due to its use in a large variety of domestic and industrial piping as a thermal and electrical conductor. Copper substrate nanostructuration was realized by electrochemical polishing to minimize textural surface effects as such the light trapping and optical losses also. Black nickel was electrodeposited on nickel films produced by the Watts solution on nanostructured C81100 copper due to their good optical properties and low cost. The nanostructured black nickel layer presented a thickness around \((2.9 \pm 0.1) \mu m\) and a higher selectivity of \(\alpha/\varepsilon = 11\), against \(\alpha/\varepsilon = 8.9\) of the non structured condition. The nanostructured black nickel presented a higher concentrated grain range size and lower nanometric RMS, a diameter deviation of 17 nm against 42 nm for the non structured condition. AFM and optical results confirmed that the nanometric size of black nickel grains and their grain size standard deviation are decisive factors to decrease the emittance and increase the final selectivity.

Key-Words: Ceramic-matrix composites (CMCs); nano particles; atomic force microscopy; infrared (IR) spectroscopy; scanning electron microscopy (SEM)
1 Introduction

Nanostructured materials are a new class of engineering materials with specific properties and structural length between 1 and 100 nm, which can be produced by a variety of different methods. Nanometric and submicrometric systems are being studied as actuators, sensors, micromotors, and frictionless gears using magnetic materials, in fabrication of nanostructured magnetic material and high performance cermet solar selective surfaces for solar energy applications, such as a solar absorber [1, 2].

Renewable energies from natural resources such as sunlight, wind, rain, tides, and geothermal heat represent answers to decrease climate changes due to harmful pollutant emissions from conventional energy sources (petrol, coal and others). However, solar thermal energy has probably the greatest potential, compared to other renewable energy resources, because the energy coming from the sun is the most powerful, cleanest and stable source [3-7].

Absorber coatings such as black nickel, black chromium and black cobalt have been applied in fairly efficient solar collector surfaces. Several techniques, such as vacuum techniques (sputtering, electron beam, chemical vapor deposition, etc.), sol-gel, electroless deposition (catalytic reduction process) are currently used to produce solar absorber surfaces. However, the desired characteristics of the solar absorber coating may be better controlled by direct electrodeposition such as their nanostructuration [2, 10]. The synthesis of nanomaterials requires an atomistic deposition process and extreme control over the deposition. Despite the fact that vacuum techniques have been used almost exclusively to produce these materials, electrochemical deposition, that is also an atomic deposition process, can be used to synthesize nanocomposites, and has generated a great deal of interest in recent years. The electrodeposition advantages against vacuum techniques are basically as follows [11]:

a. Rapidity;
b. Low cost;
c. Free from porosity;
d. High purity;
e. Industrial applicability;
f. Potential to overcome shape limitations or allowing the production of free-standing parts with complex shapes;
g. Higher deposition rates;
h. Ability to produce coatings on widely differing substrates;
i. Ability to produce structural features with sizes ranging from nm to μm;
j. Easy to control alloy composition;
k. Ability to produce compositions unattainable by other techniques;
l. The possibility of forming of simple low-cost multilayers in many different systems, e.g. Cu/Ni, Ni/Ni–P etc;
m. No post-deposition treatment.

Advantages of copper substrate for selective coatings in solar applications are as follows: longer life or durability in piping systems suitable for heating fluids up to 85°C, higher thermal and electrical conductivity (lower energy losses) and low maintenance costs. Beside these advantages, copper tubes are the standard plumbing material for potable water and heating systems in most European countries [12]. Other choices are chemical affinity and well know processes and reactions [12, 13]. A thin layer of nickel is plated to the copper to improve wear resistance and to prevent the oxidation of copper, besides promoting better black nickel adhesion [13].

Mid-temperature absorber coatings are summarized in Table 1, with comparative results of the selectivity ratio (α/ε), with the emittance reported at 100 °C [α/ε (100 °C)] (emittance measurements made by the Gier-Dunkle instrument are measured at room temperature) [2].

A black nickel’s cermet solar mid-temperature absorber can be applied onto various metal substrates using an electroplating technique. Black nickel’s cermet electrodeposits are composed of a nickel-rich co-deposit of nickel and zinc that is formed from the reduction of thiocyanate and leads to the incorporation of sulfide in the deposit at about 1 to 2 mA/cm² [14]. The mechanism of dark blackening was attributed to the deposition of these sulfide particles in the Ni-Zn alloy [1]. This sulfide ceramic layer with metallic inclusions (or cermet) acts as a selective surface. The presence of reflective particles at the infrared spectrum inside the ceramic bulk, increase the efficiency of solar energy conversion into thermal energy in thin films of metal–dielectric composites, like nanoporous nickel oxide (NiO) with Ni inclusions [14, 15]. Different groups have modified the electrodeposition bath and process to produce coatings with α/ε (100 °C) of 0.88-0.96 / 0.03-0.10, for temperatures below 200 °C. Black nickel can degrade in humid environments and with exposure to temperatures of 200 °C and is therefore not applicable for concentrating solar power applications (CSP). Kennedy reported that by incorporating topological micrometric roughness into the Maxorb’s black nickel, they enhanced the solar selectivity α/ε (100 °C) = 0.97/0.08 of their black nickel, and the texturing effect (roughness coherent with sunlight wavelengths increases absorptance due
to the topographic light trapping). Black Crystal™ or Black Forest™, are non-oxidized metallic Ni-Sn alloy solar-selective coatings on a copper substrate. Nearly all other black nickel solar-selective coatings contain oxides of nickel. Their high solar-absorbing characteristics, \( a/\varepsilon \ (100 \, ^\circ \mathrm{C}) = 0.92-0.98/0.08-0.25 \) with a thermal stability up to 300\(^\circ\)C, are a result of the micro-surface light-trapping morphology. This coating is produced by combining two processes: the electrodeposition of the crystallographic metallic alloy and applying a sol-gel overcoat. It has been developed jointly by Energy Laboratories, Inc. (ELI) in Jacksonville, Florida, and Sandia National Laboratories. This work is being done under a cooperative research and development agreement (CRADA) and is funded by both the U.S. Department of Energy (DOE) CSP and Solar Buildings Programs. The black nickel is reported by Kennedy as not appropriate for deployment in evacuated tube-type systems [2].

Black chrome (Cr-Cr2O3), an electrodeposited Cr-Cr2O3 cermet on Ni, Fe, Cu, stainless-steel substrates, has an \( a/\varepsilon \ (100 \, ^\circ \mathrm{C}) \) of 0.97/0.09 for temperatures below 300 \(^\circ\)C, being produced by MTI on Ni-plated Cu in the United States, by ChromeCoat of Denmark on copper, and on stainless-steel by Energie Solaire in Switzerland. Kennedy reports that a layer of Ni between the substrate and black chrome coating gives better stability up to 400\(^\circ\)C. Oxidation of the metallic Cr crystallite and densification of the crystallites primarily cause the degradation of the selective coating, and high temperatures produce, atomic nickel diffusion from the substrate and consequently optical degradation [2]. Black chrome solar selective films can be modified by mixing molybdenum, up to 20% of the chromium content. Absorpance is stable for an Mo/Cr ratio of 0.6% at a value of 0.95 for 146 hours up to 425\(^\circ\)C in air. Studies with a reactive sputtering deposited black chrome with \( a/\varepsilon \ 0.92-0.96 / 0.05-0.08 \) and thermal stability of 300-400 \(^\circ\)C, are reported as an alternative method by Yin [16]. Black chrome is reported by Kennedy as not appropriate for deployment in evacuated tube-type systems [2].

Stable nickel (Ni)-pigmented alumina (Al2O3) cermet selective surface coatings on aluminum substrates, intended for flat-plate collectors, are widely reported, with \( a/\varepsilon \ (100 \, ^\circ \mathrm{C}) \) of 0.85-0.97/0.08-0.21 for 300 \(^\circ\)C< T <500 \(^\circ\)C, and are commercially produced by TeknoTerm Energi in Sweden and Showa in Japan. They are made by the phosphoric anodic anodization of aluminum whose pores are impregnated with Ni, but other metals such as V, Cr, Co, Cu, Mo, Ag, Si, and W can be used [2, 15]. The lifetime of this selective surface is shortened by exposure to high temperature, humidity, and atmospheric pollution such as sulfur dioxide and abrasion also. The addition of a mechanically stable transparent coating reduces the degradation due to abrasion, high temperature, weathering, and chemical attacks. The nickel-pigmented alumina is reported by Kennedy as unlikely to be suitable for CSP applications [2].

For nucleation in electroplating, equation 1 describes Avrami’s relationship of the current (i) versus time (t) [15] that can be used for instantaneous nucleation under steady-state. This equation can be applied for a black nickel absorber and proves that the electric current is proportional to the square root of time, conducting to instantaneous nucleation [17-19].

\[
i = z \cdot F \cdot D^{1/2} \cdot N \cdot K \cdot t^{1/2} \tag{1}
\]

For black nickel electrochemical reactions, in the beginning of electrolysis, nickel, nickel–zinc alloy and/or zinc are deposited and hydrogen gas is released from the surface. Nonetheless, it decreases during the process due to over voltage of the metals. The increase in alkalinity at the metal solution interface results on the formation of nickel and zinc complex ions, interfering on the metallic cationic reduction and deposition of thiocyanate. The deposition of black nickel sulfate ions and thiocyanate on the metal surface lowers the over voltage of hydrogen to nearly the same value as in the beginning of the process, and the cycle is then repeated [20].

A solar absorber uses ultraviolet-visible-near infrared (UV-VIS-nIR) and mid infrared (mIR, thermal infrared). Solar absorptance and thermal emittance are the two main parameters for characterizing the spectrally selective nature of solar absorbing coatings at specific wavelengths’ ranges. The solar absorptance, is the weighted fraction between absorbed radiation and incoming solar radiation (in the solar wavelength range) and can be calculated by 100 less the reflectance (in %). The emittance is described as the ability of a surface to radiate thermal or infrared radiation (mIR, thermal or mid infrared wavelength range) and can be calculated by 100 minus the reflectance (in %). Selectivity is the comparative fraction between absorptance and emittance. The best selective absorbers present selectivity values over 10, denoting higher sunlight energy absorption and lower thermal energy losses [21].

The optical characteristics of nanostructured and non nanostructured electrodeposited black nickel were compared by atomic force microscopy, scanning
electron microscopy and optical UV-VIS-nIR and mIR spectrophotometry for understanding the nanostructuration effect in their optical characteristics.

2 Experiments

The proposed absorber samples were processed for black nickel coating by a standard sulphamate electrolytic solution using the following sequence of operations:

1) Nanostructuration of metallic substrates: mechanical unidirectional polishing (P1200) of C81100 copper substrates (1x1 cm²) [22]; copper electrochemical polishing (electropolished) in 85 %v/v H₃PO₄ a 1750 mV (DC) for 180 seconds (3 x 60 seconds), only for nanostructured sample [23, 24];

2) Electrodeposition of the solar absorber coating: the nickel underlayer deposition by nickel Watts bath, 2 mA/cm² for 5 minutes; the black nickel absorber coating by Fishlock bath, 0.2 mA/cm² for 15 minutes [13], on nanostructured and non structured samples.

3 Results and Discussion

3.1. Morphology: Electron Microscopy with Microanalysis Energy Dispersive X-Ray Spectroscopy (SEM with EDS)

Fig. 1. Nickel Watts cross-section image: (a) SEM: 10 000 x and (b) EDS.

The surface analysis of EDS for black nickel nanostructured and non structured coating, Fig. 3b, showed the presence of zinc, nickel, sulfur and carbon in the black nickel layer. Fig. 3a shows that the black nickel nanostructured surface is very smooth with some discontinuities. Contrarily, the non nanostructured black nickel, presented higher peaks or valleys from the mechanical unidirectional P1200 polishing. The discontinuities of the nanostructured condition can be explained by nickel tensional surface behavior. A smooth surface is a necessary condition to produce creeping (belt slip) [25, 26] and grains; on the other hand, the walls in the non structured sample come from peaks of polishing. The intense copper signals in Fig. 1b for non structured black nickel were due to the higher peaks than in nanostructured black nickel. The presence of higher peaks increases the current density, modifying local electrodeposition [27, 28]. The non nanostructured black nickel presented a stronger EDS signal for nickel (Fig. 3b), that was indicative of higher deposition rate than for nanostructurated black nickel. However, the black nickel nanostructured stressional behavior did not affect the adhesion of black nickel coating.
3.2 Optical Analysis – Spectrometry UV, VIS, nIR and mIR

Solar absorptance and thermal emittance are the main parameters to compare the optical properties of solar absorbing coatings. Fig. 4a shows reflectance (%) versus wavelength (μm) of the nanostructured black nickel, the non structured black nickel and an ideal solar selective surface. Fig 4a shows that all black nickel cermet conditions (nanostructured and non nanostructured) behave close to an ideal selective material, with the best values for the black nickel - see Table 1.

Table 1. Mid-temperature of some black selective surfaces [2].

<table>
<thead>
<tr>
<th>Material</th>
<th>Fabrication Method</th>
<th>Absorptance ((\alpha))</th>
<th>Emittance ((\varepsilon)) (100°C)</th>
<th>Commercial Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black nickel NiS-ZnS [2]</td>
<td>Electrodeposition/Sol-gel</td>
<td>0.92 - 0.98</td>
<td>0.08 - 0.25</td>
<td>Black Crystal</td>
</tr>
<tr>
<td>Black nickel Ni-Sn[2]</td>
<td>Electrodeposition/Sol-gel</td>
<td>0.97 - 0.98</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Black copper BiCu-Cu-CuO :Cu [2]</td>
<td>Electrodeposition/Sol-gel</td>
<td>0.95</td>
<td>0.09</td>
<td>MTI ChromeCoat Energie Solaire</td>
</tr>
<tr>
<td>Black chrome Cr-Cr2O3 [2]</td>
<td>Electrodeposition</td>
<td>0.97</td>
<td>0.09</td>
<td>MTI ChromeCoat Energie Solaire</td>
</tr>
<tr>
<td>Black chrome [2]</td>
<td>Electrodeposition</td>
<td>0.96</td>
<td>&lt; 0.30</td>
<td>TeknoTerm Energi Showa</td>
</tr>
<tr>
<td>Ni-NiOx  [2]</td>
<td>reactive sputtering</td>
<td>0.96</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Ni pigmented Al2O3 [2]</td>
<td>Anodization</td>
<td>0.85 - 0.97</td>
<td>0.08 - 0.21</td>
<td></td>
</tr>
</tbody>
</table>

The ideal selective surface has zero reflectance (absorptance \(\alpha = 1 - \text{reflectance} = 1 \) or 100 %) between 0.3 and 2.5 μm and unity reflectance (emittance \(\varepsilon = 1 - \text{reflectance} = 0 \) or 0%) in the infrared region, between 2.5 and 25 μm [2]. Fig. 4b presents the values of absorptance and emittance for each temperature (K) and range of wavelength (μm). In Fig. 4b, the nanostructured condition presents \(\alpha/\varepsilon = 0.977 \) (450 K) / 0.089 (300 K), for wavelengths between \(\lambda = 300 - 2500 \) nm, and the non nanostructured an \(\alpha/\varepsilon = 0.964 \) (450 K) / 0.110 (300 K) for \(\lambda = 2500 - 25000 \) nm. Fig. 4b bar graph was used to show how optical properties \(\alpha, \varepsilon \) and \(\alpha/\varepsilon \) change over nanostructuration conditions. Fig. 4b bar graph displays data against cumulative properties, with the properties in each nanostructuration condition combined and displayed as subgroups. In Fig. 4b, the absorptance for both structuration conditions for \(\lambda = 300 - 2500 \) nm shows a similar relative weight between both conditions of nanostructuration, thus the absorptances of 96.4 % (450 K) of the non nanostructured condition and 97.7 % (450 K) of the nanostructured condition are equivalent. The emittance curves for \(\lambda = 2500 - 25000 \) nm (300 K) present different behavior between nanostructured and non nanostructured conditions (Fig. 4a and bar graph, Fig. 4b): emittance presents a higher influence than absorptance in the increasing of selectivity with nanostructuration. The absorptance decreases from 11 % (300 K) in non nanostructured condition to 8.9 % (300 K) in nanostructured condition - Fig. 4b. Therefore, nanostructuration increases the selectivity from 8.9 in non
nanostructured condition to 11% in nanostructured condition, mainly due to the decrease of emittance.

Fig.4. (a) Solar reflectance of black nickel coatings (λ = 300-2500 nm, 450 K) and mIR reflectance of black nickel coatings (λ = 2500-25000 nm, 300 K) and (b) stack bar graph of black nickel coatings optical properties.

3.3 Topography and Physical Analysis: Atomic Force Microscopy and Magnetic Force Microscopy

AFM micrometric image of samples - Fig. 5a and Fig. 5b - compare the P1200 polished and electropolished samples and show the Nanostructuration effects on the surface of the electropolished copper plates via a multistep method. The JPK™ root mean square roughness (RMS) deviation has decreased from 114.6 nm (submicrometric) in the mechanical polished surface to 24.5 nm in the electropolished surface. Also, the JPK™ maximum peak height is reduced from (504.1 ± 0.1) nm (mechanical polished surface) to (39.8 ± 0.1) nm (electropolished surface). Furthermore, a better height distribution in the electropolished copper surface was registered. Thus, JPK™ AFM analysis results show that copper bulk was topographically nanostructurated.

Fig.5. AFM 20 x 20 µm images and statistical JPK™ roughness of the surface nanostructuration of (a) copper mechanical P1200 polished with and (b) copper electropolished at 1750 mV (DC), in H3PO4 85 % v/v for 180 s.

To confirm the dimensions of the black nickel coating grain size, phase contrast and topography scanning images were performed with SPIP™ image analyses. In Fig. 6c and 6e, AFM SPIP™ parameters of the black nickel absorber indicate the presence of smaller and some periodic nanometric grains for all conditions. In Fig. 6c and 6e, RMS and maximum height of the nanostructured and non nanostructured topography are lower than sunlight wavelengths and therefore, the surface texturing effects related by Kennedy [2]; this consideration means that sunlight absorbing effect in the surface are similar. Fig. 4b showed similar absorbance for both conditions too. However, in Fig. 6c and 6e, the nanostructured black nickel presented a higher concentrated grain range size, [29] some SEM morphological isotropy and lower nanometric RMS, a roughness deviation of 17 nm against 42 nm for the non structured condition.

Fig.6. Black nickel: (a) AFM 2 x 2 µm topography and (b) AFM 2 x 2 µm phase contrast image and (c) SPIP™ diameter grain size and JPK™ roughness for the nanostructured black nickel cermet, (d) AFM 2 x 2 µm topography and (e) AFM 2 x 2 µm phase contrast image and (f) SPIP™ diameter grain size and JPK™ roughness for the non nanostructured black nickel cermet.

The JPK™ AFM topography image presents a maximum height of 65.48 nm for the non nanostructured in figures 6a and 6c to 48.07 nm for nanostructured in figures 6d and 6e. The JPK™ AFM phase contrast presents a mean particle size
roughness of 94 ± 42 nm and a mode of 25 nm for non nanostructured in figures 6b and 6c to 46 ± 17 nm for nanostructured condition, and a mode of 24 nm in figures 6d and 6e. These topography and the grain size results in figures 6c and 6f confirm the nanostructuration of the black nickel absorber coating (nanometric distribution of topography and contrast phase of black nickel grains) in both conditions, but the nanostructured condition has lower values of grain size (diameter) as shown in Fig. 6c and 6e.

There is a correlation between optical properties, roughness and grain size, when comparing results from the atomic force microscopy (AFM) with the optical spectrophotometry (figures 4b and 7). The results for surface roughness of the black nickel shown in figures 6c, 6f and 7 show the same JPK™ mean roughness of 0.01 nm, and a root mean square (RMS) roughness deviation from 14.88 nm in non structured condition to 10.92 nm in nanostructured condition; this decrease in RMS deviation in nanostructured condition coincides with a small improvement of absorptance - figures 4a, 4b and 7. However, the grain size difference could justify the increase in selectivity in nanostructured condition - figures 4b and 7 - due to the decrease in emittance in the nanostructured condition. The lower grain sizes increase the specific surface area in nanostructured condition and improve selectivity, considering equivalent absorptance conditions – Fig. 4b and Fig. 7.

Besides, in Fig. 8c a magnetic domain structure is presented by the MFM trace lock-in phase image with hoover (lifting in) of 35 nm; this image presents a SPIP TM AFM in Fig. 8d estimate mean diameter particle size of 31 ± 16 nm and mode diameter particle size of 6 ± 16 nm. These nanometric particles were attributed to the ferromagnetic metallic nickel, as nickel is found in EDS analysis – Fig. 3b. Fig. 8c trace lock-in-phase in hoover of 35 nm shows a one-domain structure, “round-up” points nanometrically distributed lock-in phase image as observed by Xiansong Liu [31]. Lock-in phase at lifting in 35 nm of the surface correspond to an indicative presence of ferromagnetic metallic nickel in the black nickel cermet matrix NiS-ZnS [28]. Therefore, the black nickel cermet behavior corresponds to a strong absorption in the solar region, and a high reflection in the IR region, due to inter-band transitions related to NiS-ZnS in combination with small metal particles.

Fig. 8. MFM images with lifting in of 35 nm with JPK™ roughness and AFM SPIPTM diameters. (a) MFM images 1 x 1 µm of the height (topography profile), (b) retrace lock-in phase image (c) trace lock-in phase image and (d) SPIPTM diameter grain size and JPK™ roughness of the black nickel coating nanostructured coating.

4 Conclusions

The SEM cross section images from photomicrography of the black nickel, showed a tandem with four compositional distinctive regions or layers named as: the acrylic skeleton, the black nickel layer, the nickel Watts underlayer and the copper...
bulk. The surface analysis of EDS for black nickel nanostructured and non structured coating, showed the presence of zinc, nickel, sulfur and carbon in the black nickel layer. It was also shown that the black nickel nanostructured surface is very smooth, with some discontinuities due to nickel tensional surface behavior, and the non nanostructured black nickel presented higher peaks or valleys from the mechanical unidirectional P1200 polishing. The black nickel nanostructured stressional behavior did not affect the adhesion of black nickel coating. AFM images confirmed the success of the surface nanostructuration and the black nickel coating morphology and grain size. The copper bulk RMS roughness deviation has decreased from 114.6 nm (submicrometric), in the mechanically P1200 polished surface, to 24.5 nm in the electropolished surface (copper nanostructured condition), and the black nickel maximum height of 65.48 nm from the not nanostructured to 48.07 nm of the nanostructured, with a mean particle size of 46 ± 17 nm mean roughness and a mode of 24 nm from the not nanostructured to 94 ± 42 nm of the nanostructured condition. These results of topography and grain size for nanostructured condition confirm the nanostructuration of the black nickel absorber coating (nanometric distribution of topography and contrast phase of black nickel grains).

EDS spectrum results show that the black nickel is a coating of zinc, nickel, sulfur and carbon atoms, since MFM analysis detected the presence of ferromagnetic compound that was attributed to the metallic nickel. The presence of metallic nickel improves emittance of the black nickel due to the high reflectance in infrared wavelength.

The results of solar absorptance, thermal emittance and selectivity indicate that the optical parameters of the absorber samples are affected by nanostructuration of the black nickel. The black nickel nanostructured sample presented a higher selectivity of 11, against 8.9 of the non structured condition. AFM and optical results confirmed that the nanometric size of black nickel grains and their grain size standard deviation are decisive factors to decrease the emittance and increase the final selectivity. The black nickel nanostructured optical property is close to the best results of some black selective surfaces.

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