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Structural and optical properties of copper-coated substrates for solar thermal absorbers

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ABSTRACT

Spectral selectivity, i.e. merging a high absorbance at sunlight wavelengths to a low emittance at the wavelengths of thermal spectrum, is a key characteristics for materials to be used for solar thermal receivers. It is known that spectrally selective absorbers can raise the receiver efficiency for all solar thermal technologies. Tubular sunlight receivers for parabolic trough collector (PTC) systems can be improved by the use of spectrally selective coatings. Their absorbance is increased by deposing black films, while the thermal emittance is minimized by the use of properly-prepared substrates. In this work we describe the intermediate step in the fabrication of black-chrome coated solar absorbers, namely the fabrication and characterization of copper coatings on previously nickel-plated stainless steel substrates. We investigate the copper surface features and optical properties, correlating them to the coating thickness and to the deposition process, in the perspective to assess optimal conditions for solar absorber applications.

1. Introduction

The use of a low-intensity source like sunlight for energy generation requires an efficient system to concentrate and capture radiation and to transfer the energy to the exchange fluid. Sunlight is abundant, renewable and free of charge. Therefore the development and diffusion of solar energy exploitation is a key issue for the future. However, at present solar energy technologies are generally affected by an efficiency not high enough and by a high cost, making them not fully competitive over conventional fossil fuels yet. Thus, it is clear that both increasing the efficiency and reducing the cost is mandatory to promote solar energy exploitation. Materials utilized in different solar collector architectures are selected according to the required working temperature [1] and especially the material constituting the receiver is a key component for all collector schemes [2]. Systems operating at mid-temperatures (i.e. using fluids at about 200 ÷ 300 °C) and in particular parabolic trough collectors (PTCs) offer several advantages in comparison with conventional flat plates thanks to their higher efficiency and reduced receiver surface. In these systems the incident solar radiation is converted into heat either by direct absorption in a heat transfer fluid flowing trough transparent tubes (a black liquid [3] and, more recently, a nanofluid [4–9]) or, in the majority of cases, by sunlight absorption by blackened or specially developed absorbing surfaces that collect the solar energy and transfer it to the fluid. The characteristics which are required to the absorber surface are chemical and physical stability at the operating temperatures and good performances in terms of energy efficiency.

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Moreover a production process characterized by a low cost and a high repeatability is highly desired, as it should promote a large scale diffusion. Several direct industrial applications, like Direct Steam Generation (DSC) and Solar Heating and Cooling (SHC), could exploit mid-temperature solar energy as energy source. This interest drives the research of novel technologies focused on this market sector where the technologies developed for systems operating at higher temperatures (e.g. CSP plants) cannot be used.

Electrodeposition techniques are a promising route to obtain surfaces with tailored optical characteristics and are known in particular for coloring metallic substrates [10]. Black nickel coatings have excellent optical properties, as they are strongly absorbing in the sunlight spectral region, with a high absorbance $\alpha \approx 0.88 \div 0.96$ and a low thermal emittance $\varepsilon \approx 0.10 \div 0.15$, but they are not physically and chemically stable at temperatures $T > 200\ ^{\circ}C$ [11,12]. Black chrome coatings show a slightly lower sunlight absorption in comparison with black nickel ($\alpha \approx 0.90 \div 0.92$; $\varepsilon \approx 0.10 \div 0.15$) but they remain stable up to 300 °C [13]. However, a relevant drawback correlated to chrome electrodeposition is represented by pollution derived from Cr^{6+} ions [14,15]. Because of that, the technological development of these processes underwent a sharp slowdown since '90 [16–18]. Only with the advent of new studies about Cr^{3+} baths, since the beginning of 2000's, the electrodeposition processes have found new interest in mass production of components for thermal solar plants. To obtain a good coating by black chrome, a preliminary deposition of a nickel layer on the substrate is needed to ensure a better chrome adherence to the surface [19] and an improved wear and corrosion resistance [20]. Moreover this creates an "absorber/reflector tandem" having both the high solar absorbance of the black exterior deposit and the low thermal emittance of the metallic inner coating [20]. Recently we investigated morphological and optical properties of nickel substrates [21]. However, copper coatings are known to be possible substrates for black chrome depositions as well [17,22,23]. In addition, preliminary tests have shown that obtaining black chrome deposition on copper is very easy and that the black layer has great uniformity and adherence. For this reason, in the present work we show the realization and systematic study of copper substrates, aimed to assess their suitability as low-emittance intermediate coating for further black chrome deposition. We investigated morphological and optical properties as a function of the bath parameters and coating thickness.

2. Experimental

Substrates for copper electrodeposition have been chosen to be stainless steel AISI 304 samples with a preliminary nickel coating (Wood bath for Ni [21], 0.9 μm Ni thickness). The composition of Cu sulphate acid bath [25,26] was $CuSO_4 \cdot 5H_2O$ 225 g l^{-1} and H_2SO_4 concentrated 33 g l^{-1}. Other parameter were: laminated Cu anodes, room temperature, current density 2–5 A dm^{-2}. In detail, two consecutive depositions have been carried out, the first one for times from 0.5 to 14 min with current density 3.45 A dm^{-2} (results shown in Fig. 1), and the second one with 0.51 A dm^{-2} for 5 and 10 min, as proposed in Ref. [27].

Thicknesses have been measured with Calotest CSM and optical microscope Nikon Eclipse LV 150, by means of the image analysis. Structural characterization has been performed using a scanning electron microscope SEM "Zeiss Merlin". A Hommel Tester W55 (Jenoptic) has been used for measuring the roughness. The hemispherical reflectance spectra from 0.25 to 16 μm wavelength have been acquired using two experimental apparatuses: a double-beam spectrophotometer (Lambda 900 by Perkin Elmer) equipped with a 150 mm diameter Spectralon®-coated integration sphere for the 0.25–2.5 μm wavelength region (this setup is also suitable for measuring the purely diffuse reflectance and thus obtaining the specular component as a difference) and a FT-IR "Excalibur" Bio-Rad spectrophotometer, equipped with a gold-coated integrating sphere and a liquid nitrogen cooled detector for the wavelength region 1.8–16 μm. For diagnostic purposes we acquired also the specular reflectance spectra of samples, extending the investigated spectral region up to 40 μm wavelength. The Excalibur spectrometer, equipped with the proper accessory for specular reflectance measurements, allows to reach 25 μm

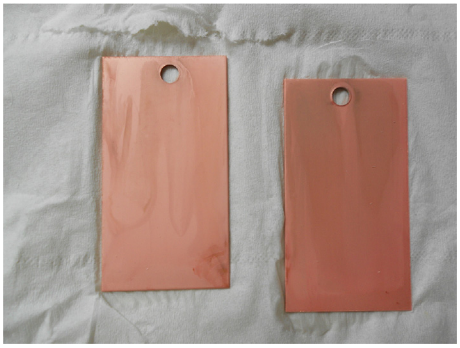

Fig. 1. Cu-coated samples for current density 3.45 A dm^{-2}, deposition time 1 min.