Optical characterization of Zn coatings deposited on low carbon steel substrates

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Abstract. We studied the optical reflectance profile of zinc layers with thickness of 2-10 μm electrodeposited on low carbon steel in the spectral range of solar radiation (0.3 - 2.5 μm) and in the thermal infrared (2.5 - 15 μm). Spectral selectivity is an important parameter of the solar absorbers used in solar thermal collectors. It is defined by low reflectance in the range 0.3 - 2.5 μm, and high reflectance in the thermal infrared, 2.5 - 15 μm. The Zn coatings are thick and their surface is rough. If the surface features size is in the order of the visible wavelengths, then absorption of light at the surface is possible. The investigations revealed the formation of ZnO on the Zn coating surface. The Raman study showed a weak peak around 512 cm⁻¹, which can be attributed to the ZnO oxide phase. The longer wavelengths penetrate the oxide surface and reach the bulk part of the Zn coating where they are reflected. As a result, a step-wise profile is expected in the reflectance spectrum within the 0.3 -15 μm range, with a change from a comparatively low reflectance in the visible to a high reflectance in the infrared.

1. Introduction
Electrodeposited zinc coatings on steel find wide practical utilization in various industrial applications [1–3]. Under atmospheric conditions, zinc corrodes by a factor of up to 100 less than steel [4]. This metal is also less noble compared to iron at ambient conditions and will predominantly corrode to protect the substrate [5]. Various techniques have been applied for improving the zinc coatings performance - alloying with other metals, conversion coatings prepared from environmentally friendly solutions [6], composite coatings, incorporating organic or non-organic micro- or nano-sized particles etc. [7-9]. Steel is a material used very often in solar absorbers. Many studies have been conducted on spectrally selective solar absorbing coatings deposited on stainless steel. The cost-effectiveness of the overall technology would be raised if a technology with ordinary steel is developed ensuring non-corrosive properties of the solar absorbers system by means of a coating (in the present study low carbon steel is used). At the same time, the absorber efficiency will increase if this coating exhibits a certain degree of spectral selectivity of the reflectance. APCVD deposited black Mo [10] has been

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subjected to long-term testing at 500°C for 2000 hours. Other, less expensive, technologies have been developed and reported. In [11], the authors considered chemical-solution derived spectrally selective absorbers and employed an antireflection (AR) approach to develop optically selective coatings by deposition of silica, alumina and mixture of silica-titanium. In order to make the coatings more flexible, an organic compound is often added [12] to the film structure, thus forming a hybrid film structure. In the technology considered here, an organic substance was added to fill the large pores of the coating with anticorrosion purposes and, in some cases, to smooth the shiny surface.

The technological process used is usually employed for implementing anti-corrosive coatings. The process is simple, fast, environmentally friendly and suitable for large-scale applications. We introduce below some basic information for solar absorber systems. The spectrally selective optical coatings are characterized by a coefficient of absorptance of the solar radiation and by acoefficient of thermal re-radiation, called in short solar absorptance and thermal emittance. The purpose is to make the solar absorber system (a substrate with a coating) absorptive in the range where sun radiates (0,3 - 2,5 μm). Since the solar absorber systems are not transparent (the substrate is metallic), the solar radiation is either reflected by the coating, or absorbed in the optical system (a substrate covered by a coating):

\[ 1 = R(\lambda, T, \theta, \phi) + \alpha(\lambda, T, \theta, \phi). \]  

(1)

Solar radiation falls under angles \( \theta, \phi \) on the surface of a coating and is absorbed or scattered at different angles in the hemisphere above the coating surface. According to Kirchhoff’s law, at thermodynamic equilibrium with the environment, the spectral coefficient of absorption and the thermal emittance at a certain wavelength are equal, \( e(\lambda, T, \theta, \phi) = \alpha(\lambda, T, \theta, \phi) \); equation (1) can then be written as:

\[ 1 = R(\lambda, T, \theta, \phi) + e(\lambda, T, \theta, \phi). \]  

(2)

It is obvious that if a coating reflects highly in the infrared, it will not emit in this spectral range.

2. Experimental details

The coatings were electrodeposited at cathodic current density of 2 A/dm² on low-carbon steel substrates (20×10×1 mm) from electrolyte containing ZnSO₄.7H₂O (150 g/l), NH₄Cl (30 g/l), H₃BO₃ (30 g/l) and two additives: AZ1 (wetting agent – 50 ml/l) and AZ2 (brightener – 10 ml/l).

Normal reflectance and full reflectance spectra were measured by a Shimadzu UV-VIS-NIR spectrophotometer. FTIR spectra were obtained by a FTIR IRPrestige-21 spectrometer at a high signal to noise ratio 40000:1, accumulation 200 scans, high-energy ceramic light source, resolution 4 cm⁻¹. The FTIR system covers the spectral range 350 – 7300 cm⁻¹. An SRM 8000 reflectance attachment was used. The Raman measurements were performed on a Raman spectrophotometer equipped with a He-Ne laser (633 nm, laser power 7 mW) and an objective ×50, in the range 100 - 4000 cm⁻¹ and with accumulation time 30 s × 3 (for N1 and N2) and 50 s × 3 (for steel plates).

3. Results and discussions

The samples were optically characterized by measurements of the reflectance spectra in the range 0.3 – 2.5 μm and in the infrared range of 1.3 – 25 μm. Two sets of samples were investigated denoted as 82 (Zn:ZnO coatings with a thickness of about 10 μm), and 83 (Zn:ZnO coatings with a thickness of about 2 μm), each containing 10 samples. Figure 1 illustrates the very high (73-80%) infrared reflectance of almost all samples. Sample 9 with the highest (95%) IR reflectance (the yellow line in figure 1) exhibited the lowest \( R \) in the visible (the blue line in figure 2). Selected samples, with the highest reflectance in the infrared range and the lowest one in the visible, were annealed in view of improving the reflectance profile in the range 0.3 – 25 μm.
Figure 1. Infrared spectral reflectance for samples of set 82.

Figure 3. Infrared spectral reflectance for samples of set 83.

The process causing a lowering in the visible reflectance could be light trapping at the rough surface of the coatings. If the degree of roughness is in the order of the wavelength, then absorption is possible due to the multiple reflectance of light.
between the crystallites walls. Another contribution might arise from the graded index profile of the structure air/ZnO/Zn – the light enters the optical system meeting media with gradually increasing density (air, ZnO and finally Zn surface). It is interesting to note that better selectivity is observed for samples with higher numbers, which were prepared last in order, probably because the amount of some ingredients of the solution has decreased. We present here only the first experimental results. Further studies are necessary on the dependence of the films structure, morphology, and the chemical composition on the process parameters.

The Raman spectra of selected samples with optimal properties are given in figure 5. The Raman peaks observed centered at 1339, 1598 and 2012 cm$^{-1}$ are related to structural water in the film. The Raman peak in all samples at 512 cm$^{-1}$ is attributed to the oxide phase. We envisage to conduct studies on the effect of annealing at temperatures of a few hundred degrees in order to increase the oxide fraction.

Conclusions
A very simple technological process is developed for deposition of coatings on low-carbon steel. The films possess spectral selectivity of their reflectance in the range of 0.3 – 25 μm. The investigations reveal that some of the films show a decreased visible reflectance and an increased infrared one. The selected technology is promising for the development of solar absorbing coatings. Optimization of films structure and chemical composition, as related to the process parameters optimization, will result in improved spectral selectivity.

References
[1] Brenner A 1963 Electrodeposition of Alloys. Principles and Practice (Academic Press, New York)
[2] Zhang J, Yang Z, An M, Li W and Tu Z 1995 Plat. Surf. Finish. 82 135
[3] Vourlias G, Pistofidis N, Chaliampalias D, Pavlidou E, Patsalas E, Stergioudis G, Tsipas D and Polichroniadis E K 2006 Surf. & Coat. Techn. 200 6594
[4] Zhang X G 1996 J. Electrochem. Soc. 143 1472
[5] Marder A R 2000 Prog. Mater. Sci. 45 191
[6] Rafaey S A M, Abd El-Rehim S S, Taha F, Saleh M B and Ahmed R A 2000 Appl. Surf. Sci. 158 190
[7] Hovestad A, Heesen R J C H L and Janssen L J J 1999 J. Appl. Electrochem. 29 331
[8] Koleva D, Boshkov N, Raichevski G and Veleva L 2005 Trans. Instit. Metal. Finish. 83 188
[9] Boshkov N, Tsvetkova N, Petrov P, Koleva D, Petrov K, Avdeev G, Tsvetanov Ch, Raichevsky G and Raicheff R 2008 Appl. Surf. Sci. 254 561
[10] Gesheva K A and Chain E E 2008 Black Molybdenum Spectrally Selective Surfaces (Novapublishers N.Y.)
[11] Bostrom T K, Wackelgard E and Westin G 2005 Solar Energy Mater. Solar Cells 89 197
[12] Tadanaga K, Iwashita K, Minami T and Tohge N 1996 J. Sol-Gel Sci. Techn. 6 107