ZnO thin films on aluminized steel by spray pyrolysis

R. López Ibáñez, R. Romero, F. Martín, J. R. Ramos-Barrado and D. Leinen*

Laboratorio de Materiales y Superficie, (Unidad Asociada al CSIC), Dpto. Física Aplicada I & Dpto. Ingeniería Química, Universidad de Málaga, 29071 Málaga, Spain

Received 4 July 2005; Revised 25 November 2005; Accepted 29 November 2005

Spray pyrolysis is a low-cost technique and results in minimal waste production when using adequate precursors. The process allows the coating of large surfaces and is appropriate for adaptation into an industrial production line. The aim of this work has been to obtain, by spray pyrolysis, thin and compact ZnO films on 30 × 40 cm galvanized steel sheets heated by high frequency magnetic induction and using zinc acetate precursor in aqueous spray solution. The work includes a study of optimized deposition conditions (substrate temperature, precursor solution concentration, flow rate and spray time) controlled ex situ by SEM, XPS, XRD and UV-Vis-NIR and FTIR diffuse reflectance spectroscopy, in order to obtain an effective barrier coating with low thermal emittance when the steel is used as a base material for solar thermal devices. Our results show improved anti-corrosion performance when the substrate coverage is guaranteed, substrate temperature and deposition time being the main factors to accomplish the optical requirements of the ZnO-coated galvanized steel. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: spray pyrolysis; ZnO thin film; aluminized steel sheet; physical barrier

INTRODUCTION

Galvanized steel sheets are being tested as base materials for absorber surfaces in unglazed solar collectors to be integrated in building façades (EU project SOLABS; www.solabs.net). Because the collector will be directly exposed to the environment, it is necessary to improve its anti-corrosive behaviour. Usually a thick polymer coating or an inorganic layer could be used as an anti-corrosion barrier,1 but current chromate coatings are extremely toxic and the specific optical requirements of the collector require using a very thin film as an anti-corrosion barrier so that the thermal emittance of the whole absorber-barrier-substrate system does not increase. Without prejudice to the low thermal emittance, an improvement of the solar absorbance would be welcomed. Some metallic oxides comply with these requisites.2 On the other hand, hot-dip aluminized steel has shown adequate anti-corrosive and optical properties to be used as a base material for unglazed solar thermal devices.3 Nevertheless, it is necessary to improve its corrosion protection with a top barrier layer to delay early degradation.

Spray pyrolysis is a low-cost technique that allows coating large surfaces. In this technique, the substrate to coat is kept at constant temperature while the precursor solution is atomized over it. To avoid the oxidation of the galvanized steel, low substrate temperatures must be used. On the other hand, the oxide thin film obtained must show good adhesion to the galvanized steel and compatibility with the compounds forming the optical selective layers. Attending to these reasons, we have selected ZnO as a physical barrier. ZnO is an n-type semiconductor, with an optical bang-gap of 3.3 eV.4,5 This metallic oxide has been used as an anti-reflection layer, and as a transparent conductor.6,7 Prior to this work, we have obtained ZnO thin films by spray pyrolysis on other substrates such as fused silica, silicon or glass,8,9 as well as compact, transparent and well-adhered ZnO films on aluminized steel substrate.10 It is accepted that when the ZnO is directly exposed to moisture, it reacts with the water, resulting in the formation of zinc hydroxide. Over time, and under the influence of cyclic weathering, the final corrosion product is zinc carbonate. Zinc carbonate forms a thin, tenacious, compact, stable and water-insoluble film. This protective film serves as a barrier between the moisture and the galvanized steel underneath. Electrochemical techniques have been used to determine the anti-corrosive properties of the ZnO thin films deposited on the aluminized steel.10 In H2SO4 electrolyte solution, the corrosion rate can be measured from potentiodynamic polarization curves. This parameter is used in this work to estimate the anti-corrosion behaviour of zinc oxide layers on aluminized steel sheets in comparison with the substrate itself.

EXPERIMENTAL

For these purposes, a new spray station was specifically designed to cover larger surfaces, using previous experience in the spray pyrolysis technique. Four high frequency induction coils were employed to heat the steel, arranging them suitably to ensure a uniform thermal distribution; the substrate temperature was on trial at 200 °C and 250 °C.
Table 1. Deposition conditions of the zinc oxide thin films and their solar absorptance and thermal emittance values in comparison to substrate

<table>
<thead>
<tr>
<th>Sample name</th>
<th>S-4</th>
<th>S-6</th>
<th>S-14</th>
<th>S-16</th>
<th>S-17</th>
<th>S-22</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature (°C)</td>
<td>200</td>
<td>200</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>–</td>
</tr>
<tr>
<td>Precursor solution flow rate (ml/h)</td>
<td>840</td>
<td>1200</td>
<td>840</td>
<td>840</td>
<td>840</td>
<td>1200</td>
<td>–</td>
</tr>
<tr>
<td>Precursor solution concentration (M)</td>
<td>$2 \times 10^{-2}$</td>
<td>$2 \times 10^{-2}$</td>
<td>$5 \times 10^{-2}$</td>
<td>$2 \times 10^{-2}$</td>
<td>$5 \times 10^{-2}$</td>
<td>$2 \times 10^{-2}$</td>
<td>–</td>
</tr>
<tr>
<td>Deposition time (min)</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>–</td>
</tr>
<tr>
<td>$\alpha_{AM 1.5}$</td>
<td>0.52</td>
<td>0.52</td>
<td>0.43</td>
<td>0.47</td>
<td>0.47</td>
<td>0.46</td>
<td>0.41</td>
</tr>
<tr>
<td>$\varepsilon_{373 K}$</td>
<td>0.15</td>
<td>0.13</td>
<td>0.12</td>
<td>0.14</td>
<td>0.14</td>
<td>0.13</td>
<td>0.15</td>
</tr>
</tbody>
</table>

A four-nozzle array homogeneously sprayed the precursor solution over the substrate at a 20-cm height. Zinc acetate in bi-distilled water was used as a precursor solution at $2 \times 10^{-2}$ M and $5 \times 10^{-2}$ M concentration, being pumped at 840 ml/h and 1200 ml/h into a 2-bar air stream. The two-way-running substrate holder carried the steel sheet in and out of the spray zone at a constant velocity of 3 or 5 min as deposition time. Table 1 shows the deposition conditions of each sample. All of them were prepared on $30 \times 40$ cm$^2$ steel sheets cut from a hot-dip aluminized steel coil delivered by ThyssenKrupp Stahl. The atomic composition of the hot-dip aluminized layer was 87% aluminium, 10% silicon and 3% iron (TK-AS), covering a low carbon steel strip (TK-DX 56). A two-step cleaning procedure of the substrate was made degreasing with detergent and alcohol.

XPS analysis was carried out with a PHI 5700 equipment using Mg Kα radiation (1253.6 eV). 4 keV Ar$^+$ sputtering at a rate of 3 nm/min, as determined in Ta$_2$O$_5$, was used for in-depth analyses. High-resolution spectra of C 1s, O 1s, Zn 2p$_{3/2}$, Al 2p and Si 2p photoelectron peaks and of Zn$_{100}$ Auger peak were recorded to identify the chemical state of the elements in the coatings, and to estimate the quantitative composition of the thin films. The optical properties of the zinc oxide coatings deposited on aluminized steel were studied by diffuse reflectance spectroscopy. For the UV-Vis-NIR wavelength range, Shimadzu-3100 equipment with barium sulphate internal sphere was used, and for the MIR range a Bruker F/66-S FTIR spectrophotometer with external gold sphere was employed. The spectral reflectance ($R(\lambda)$), the incoming solar radiation for mid-European latitudes ($I_{AM 1.5}$) and the Plank black body radiation at 373 K ($I_{P 373 K}$) were used to calculate the solar absorptance ($\alpha_{AM 1.5}$) and thermal emittance ($\varepsilon_{373 K}$) values of the coatings as follows:

$$\alpha_{AM 1.5} = \frac{\int_{0.3}^{2.5} I_{AM}(\lambda)(1 - R(\lambda))d\lambda}{\int_{0.3}^{2.5} I_{AM}(\lambda)d\lambda}$$

$$\varepsilon_{373 K} = \frac{\int_{0.3}^{2.5} I_{P}(\lambda)(1 - R(\lambda))d\lambda}{\int_{0.3}^{2.5} I_{P}(\lambda)d\lambda}$$

XRD patterns were obtained by the assistance of Bragg-Brentano SIEMENS D-5000 diffractometer with CuKα radiation. The surface morphology was studied by SEM with a JEOL JSM-5300, not requiring any metallic over-coating for the as-deposited samples to be introduced in the microscope. Electrochemical measurements were made by means of a three-electrode cell with a Pt wire as counter electrode and a saturated calomel electrode (SCE) as reference. A scan rate of 20 mV/s was used. The cyclic voltammetry (CV) was performed in a 0.1 M K$_2$SO$_4$ solution containing 0.01 M K$_3$[Fe(CN)$_6$] with a potential sweep range from -0.2 to +0.7 V.

Figure 1. Diffuse reflectance spectra of the as-deposited ZnO thin films on aluminized steel in comparison with the substrate itself.
Table 2. XPS atomic concentration and modified Auger parameter of the ZnO thin films

<table>
<thead>
<tr>
<th>Sample</th>
<th>S-4</th>
<th>S-6</th>
<th>S-16</th>
<th>S-22</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (at.%)</td>
<td>22</td>
<td>21</td>
<td>43</td>
<td>23</td>
</tr>
<tr>
<td>O (at.%)</td>
<td>4</td>
<td>38</td>
<td>13</td>
<td>47</td>
</tr>
<tr>
<td>Al (at.%)</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-4</td>
</tr>
<tr>
<td>Si (at.%)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn (at.%)</td>
<td>32</td>
<td>31</td>
<td>18</td>
<td>30</td>
</tr>
<tr>
<td>Zn/O</td>
<td>-0.9</td>
<td>0.9</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>$\alpha'$ (ZnLMM)</td>
<td>2010.6</td>
<td>2010.7</td>
<td>2010.8</td>
<td>2010.4</td>
</tr>
</tbody>
</table>

of a PGSTA 30 Autolab in 0.1 M H2SO4 aqueous electrolyte, in a corrosion test cell specially designed for flat large samples with three electrodes. A platinum grid was used as a counter electrode, a saturated calomel electrode as a reference and the sample as a working electrode with a 0.79 cm² contact area to the electrolyte solution. A scan rate of 1 mV/s was fixed for measurements in [−1.0 V, +0.5 V] range, after 5 min equilibration time.

RESULTS AND DISCUSSION

The diffuse reflectance spectra of the as-deposited zinc oxide samples showed great differences for different deposition conditions in comparison with the substrate reflectance spectrum (Fig. 1). Samples prepared at lower substrate temperatures had a larger absorption band at UV wavelengths (~380 nm), related to a higher amount of oxide material deposited onto the galvanized steel. The energy of this absorption band edge (3.28 eV) was found to be in good agreement with the zinc oxide band-gap bulk values found in the bibliography. Differences in reflectance spectra were less important considering different precursor solution flow rates or concentrations. The substrate temperature is the most important variable to control during deposition, and thermal changes on the surface of the substrate can modify the coating properties. The solar absorbance values of the as-deposited samples were calculated (Table 1), revealing that a minimum coating thickness is needed to increase the solar absorbance of the substrate. In the MIR region of the diffuse reflectance spectra, no absorption bands were found related to organic compounds, and so no significant amount of precursor traces were expected to be retained in the zinc oxide coatings, performing a good pyrolysis during deposition. Thermal emittance of the galvanized steel was not increased by these highly transparent zinc oxide thin films, keeping the low-emittance behaviour for these coatings.

Substrate coverage and chemical composition were checked by XPS. Although all the thin films were deposited onto the metallic substrate, some charge effects took place during analysis, and binding energies (BE) were slightly shifted to higher values. A correction for the BE is then needed, taking Zn2p3/2 as a reference peak at 1021.8 eV. The C 1s core level of surface analysis was then found at 284.9 eV according to hydrocarbon contamination as expected for ex situ analysis. Binding energy of O 1s (530.2 eV) photoelectron peaks and Auger parameters related to ZnLMM (~2010.8 eV) indicate a zinc oxide thin film growth during pyrolysis in all the cases. Table 2 contains the atomic concentration of the zinc oxide films obtained by XPS at the surface and after 1 min 4 keV Ar⁺ surface etching. All the samples exhibit some oxygen deficiency because of non-stoichiometric zinc oxide synthesis. High-resolution O 1s photoelectron peak analysis showed two contributions in binding energy, one related to Zn−O bonds (530.2 eV) and a second one to H−O bonds (532.0 eV), in a 65 : 35 atomic relation. Nevertheless, we can conclude that no zinc hydroxide is present in the synthesized thin films as no OH stretching band was found in the IR spectra. Some carbon, less than 4 at.%, has still
been detected after 1 min 4 keV Ar⁺ sputtering, probably due to small amounts of not completely pyrolysed precursor near the film surface, not detectable by FTIR spectroscopy. Lack of aluminium from the galvanized layer in these XPS analyses can be translated into complete substrate coverage, also confirmed by scanning electron micrographs represented in Fig. 2. From the SEM observations, it could be seen that pinholes in the galvanized substrate surface were covered by the homogeneous ZnO layer. However, the surface roughness could not be smoothed by these extremely thin ZnO films. For similar ZnO coatings on hot-dip aluminized steel, a 15-nm thickness was estimated by XPS depth profiling.

The as-deposited samples were analysed by X-ray diffraction to study their structural properties. The patterns of the zinc oxide layers (not shown) consisted of three peaks, but owing to the little thickness of the ZnO thin films the reflections (100), (002) and (101) according to JCPDS data card 05-0664, corresponding to ZnO wurtzite structure. Reflections (100), (002) and (101) according to JCPDS data card 05-0664, corresponding to ZnO wurtzite structure. However, all the peaks could be identified as reflections (100), (002) and (101) according to JCPDS data card 05-0664, corresponding to ZnO wurtzite structure.

The electrochemical measurements of the zinc oxide coatings in sulphuric acid showed no significant differences on corrosion parameters for different deposition conditions, except in the case of short deposition times. Figure 3 represents the polarization curve of sample S-6 in comparison with the substrate. For the ZnO-coated substrate, the corrosion potential shifted to more noble values and the current density decreased by about ten times, both features with the substrate itself, the corrosion rate was decreased by the oxide layer. Reduction in cathodic current densities make the coating suitable for protection in an acid atmosphere as the dissolution of the metal is delayed. The electrochemical results obtained for the different tested deposition conditions make us think that the significant corrosion protection effect is due to the homogeneous and compact ZnO thin film obtained, which has filled the galvanized steel substrate holes.

CONCLUSIONS
ZnO thin films have been sprayed onto 30 × 40 cm² aluminized steel sheets. XPS results showed the formation of a very thin ZnO layer during deposition with a small contamination of organic waste from the precursor solution (less than 4 at.%). Deposition conditions have been studied and the results confirm that substrate temperature and deposition time are the main variables to be controlled. With respect to its application in unglazed solar collectors, adequate solar absorptance and thermal emittance as well as an increase in corrosion protection have been obtained for the ZnO-coated aluminized steel.

Acknowledgements
Funding from the EU project SOLABS: ENK6-CT2002-00679 are gratefully acknowledged.

REFERENCES