In-depth composition study of zirconia-coated steel sheet by XPS

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Zirconia was deposited by spray pyrolysis on large-area aluminized steel sheets using two different types of heat sources: infrared radiation or white light. XPS in-depth composition study has shown that the carbon concentration is 4 at.% when using white light but 15 at.% when using infrared radiation. This carbon is found as zirconium carbide, formed as a diluted phase in the zirconia coatings. In the case of using infrared radiation, reflectance spectroscopy revealed a partial degradation of the optical properties of the coatings due to an incomplete pyrolysis of the precursor. These findings are of direct interest for unglazed solar façade elements made of steel, in which the zirconia coating will act as a barrier layer against the degradation of the steel sheet during long-term outdoor exposure. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: ZrO₂; steel; spray pyrolysis; XPS; depth profiling

INTRODUCTION

XPS and other surface analytical techniques have often been applied in situ in order to control the different coating parameters at laboratory level. However, at industrial scale such an in situ process control is mostly impossible and coating parameters have to be optimized via ex situ analysis. Valuable information, although time consuming, can be obtained by XPS depth profiling. In this context, an XPS in-depth composition study on spray-pyrolyzed zirconia coatings on aluminized steel sheet is presented showing the capability of the technique for composition control of the coatings as a function of the processing temperature for pyrolysis. Two different systems for substrate heating, i.e. infrared radiation or white light, have been applied yielding different temperatures for pyrolysis, growth velocity and coating quality.

Previous experience with spray-pyrolyzed coatings led to the selection of zirconia as the potential barrier-layer material on steel. The steel sheet will be used as base material for unglazed solar façade elements. The barrier layer will prevent the degradation of the element subjected to ambient impact during long-term outdoor exposure, for instance, through pinholes or other defects introduced during fabrication and handling. In this work, we show that it is possible to control the quality of zirconia coatings sprayed onto aluminized steel sheet by XPS depth profiling together with complementary surface analytical techniques like SEM and diffuse UV-VIS-IR reflectance spectroscopy. From the latter, solar absorptance and thermal emittance are evaluated serving as optical quality parameters of the coatings for solar energy applications.

EXPERIMENTAL

In chemical spray pyrolysis, the precursor solution is sprayed onto the heated substrate. Two different heating systems were used: (i) a set of quartz lamps working with filaments open to atmosphere and filament temperature ~1000 K yielding mainly infrared emission; and (ii) a set of halogen lamps with filament temperature ~3000 K yielding white light. Both lamp sets were adjusted in position to an aluminized steel sheet of 1 m length and 0.4 m width (0.3 mm thick) in order to obtain an overall homogeneous substrate temperature for pyrolysis of ~523 K (250 °C) on the surface of the steel sheet. For this purpose, the steel sheet was kept moving during spraying; in case of quartz lamps (system A), at a velocity of 5 cm/s ten times through the spray zone, and in case of halogen lamps (system B), at a velocity of 4 cm/s six times through the spray zone.

Zirconium acetyl acetonate (98% purity) at a concentration 10⁻² M was used as precursor for the aqueous spray solutions. Four nozzles across the substrate at distance of 20 cm from the substrate were used, spraying at a pumping flow rate of 4 × 150 ml/h and an air pressure of 2 bar. The steel sheets were obtained from ThyssenKrupp Steel. They were hot-dip coated, fired, aluminized steel sheets with the commercial denomination FAL. The aluminized layer consisted of 10% silicon, 3% iron and the remainder aluminum. The abbreviation AS will be used to denote this layer.

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corrosion resistance of hot-dip coated steels from Thyssen Krupp Steel has been studied elsewhere.\textsuperscript{5}

Depth profiling was carried out by XPS (X-ray source: Mg $K\alpha$ (1253.6 eV), 15 kV, 300 W) combined with 4 keV Ar$^+$ sputtering with a PHI 5700 equipment. The pressure in the analysis chamber was about 10$^{-7}$ Pa. The sputter rate at 4 keV Ar$^+$ and a beam rastering of 3 $\times$ 3 mm$^2$ was assumed to be approximately 3 nm/min in oxide material, as determined in Ta$_2$O$_5$ under identical sputter conditions. Binding energies were referenced, only for original unsputtered surfaces, to the Zr 3d peak at 182.2 eV.\textsuperscript{6} The spectra were handled with PHI-Access V.6 and Multipak software, both from Physical Electronics. Atomic concentrations were determined from C 1s, O 1s, Zr 3d, Si 2p and Al 2p XPS peak areas using Shirley background subtraction\textsuperscript{7} and sensitivity factors provided by the spectrometer manufacturer (Physical Electronics, Eden Prairie, MN). Spectra extraction made from the XPS depth profiles corresponds to the spectra obtained by summarizing the measured spectra at a certain depth length (number of consecutive sputter sequences) in the profile.

Microphotography was carried out with a Jeol JSM-5300 scanning electron microscope. The samples were introduced into the microscope as obtained by spray pyrolysis, i.e. without any topcoat with gold or graphite. Cu $K\alpha$ radiation of a Siemens D 5000 diffractometer (Bragg-Brentano) was used for XRD, and it was found that all zirconia coatings prepared at 523 K by spray pyrolysis were amorphous. Spectral hemispherical reflectance measurements were made in the UV-VIS-NIR range (190–2500 nm) with a Shimadzu spectrometer provided with an internal integrating BaSO$_4$ sphere, and in the MIR range (2–17 $\mu$m) with an IFS66 from Bruker with an external integrating gold sphere of 20 cm diameter. The solar absorptance, $\alpha$, and the thermal emittance, $\varepsilon$, were determined from the reflectance measurements. $\alpha$ is the weighted fraction between absorbed radiation, $(I_{AM}(\lambda)/I_{AM}(\lambda))$, and incoming solar radiation according to the standard AM1.5, $(I_{AM}(\lambda))$, $R(\lambda)$ being the spectral reflectance.

$\varepsilon$ is the weighted fraction between the emitted radiation and the Planck black body distribution at 373 K, $(I_{P}(\lambda))$.

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

$$\varepsilon = \int_{2}^{17} \frac{I_{P}(\lambda)(1 - R(\lambda))}{\int_{2}^{17} I_{P}(\lambda)} d\lambda$$

RESULTS AND DISCUSSION

X-ray photoelectron spectroscopy (XPS)

Various AS steel sheets of 1 m length and 0.4 m width were top-coated with zirconia, either using quartz lamps (system A) or halogen lamps (system B) for heating the steel sheet. All samples were analyzed at different sites in order to check complete coverage and homogeneity of the coatings. As an example, Fig. 1 shows the XPS atomic concentration depth profiles of Film A and Film B obtained by substrate heating with quartz lamps or halogen lamps, respectively. The estimated minimum zirconia film thickness, 90 nm for Film A and 30 nm for Film B, is indicated in each profile.

![Figure 1. XPS 4 keV Ar$^+$ sputter depth profiles of zirconia Film A and zirconia Film B on AS steel sheet. The represented carbon concentration for Film A corresponds only to ZrC.](Image)
sharp because of the high roughness of the steel sheet, as can be seen in the SEM pictures (Fig. 5). After an initial decrease of the O signal due to ion-bombardment-induced chemical reduction of zirconia to lower oxidation states, a steady state situation in composition is reached, and Zr, O, and C signals remain constant until reaching the interface. This indirectly reveals a constant composition in the sprayed layer. Furthermore, C is found in relatively large amount, approx. 15 at.% in Film A and at much lower concentration, approx. 4 at.%, in Film B. In the steady state situation, this C is in the form of ZrC as can be seen by the BE of C 1s peak shown in Fig. 2, representing C 1s spectra extractions of the profiles of Film A and Film B corresponding to sputter depth from 5 to 30 min of 4 keV Ar⁺ etching. It is worth mentioning that the profile of Film A (Fig. 1) shows only the C concentration corresponding to ZrC. Further detail about the existence of C in Film A through the first minutes of 4 keV Ar⁺ etching is shown in Fig. 3. At the surface, it shows a high carbon contamination. Two main contributions can be seen, corresponding to aliphatic carbon around 285 eV and carboxylic species at 289 eV in binding energy. However, this carbon is clearly a surface contamination because it is nearly completely sputtered away by 4 keV Ar⁺ etching for 1 min. Then, after further sputtering, the C 1s signal increases again and is found around 282 eV corresponding to ZrC, however, not reaching the steady state intensity until at least 5 min of sputtering (see also the carbon profile of Film A in Fig. 1). Therefore, we think that ZrC is already formed during the film growth and not only an effect of 4 keV Ar⁺-induced phase transformation to ZrC due to C containing residuals from the precursor molecules in the zirconia film. This argument is supported by the fact that the XPS concentration profile of Film B shows a much lower carbon concentration of about 4 at.%, also as ZrC (see spectra extraction in Fig. 2). The relative decrease in C concentration shows that heating by halogen lamps is more effective in the elimination of the organics of the precursor during pyrolysis, increasing thereby the amount of Zr in the chemical composition of ZrO₂. However, still some C in form of ZrC is present in Film B. Here, it is also worth mentioning that the ratio C/Zr is equal to 20 in the zirconium acetyl acetonate precursor. Furthermore, the fact that very different zirconia layer film thicknesses are found when comparing Film A with Film B shows that the film growth velocity tuned, in that case, mainly by the different heat sources, quartz or halogen lamps, is important for the kinetics during pyrolysis of burning away the organic component of the precursor and the competitive formation of ZrO₂ and ZrC.

**Spectral hemispherical reflectance and SEM**

Figure 4 shows the spectral hemispherical reflectance measurements from 190 nm to 17 μm of Film A and Film B, and for comparison of the AS steel substrate itself. As a
Figure 4. Spectral hemispherical reflectance of zirconia Film A and zirconia Film B on AS steel sheet, and, for comparison, of the AS steel sheet itself. The solar absorbance $\alpha$ and the 373 K thermal emittance $\varepsilon$ are indicated for each surface.

Metallic surface, the reflectance of AS steel is relatively high, not changing much in the whole measured spectral range. Zirconia is a transparent, high-band-gap ceramic material. A high-quality zirconia layer should be highly transparent from visible to the MIR region. However, Film A shows two strong absorption bands, i.e. reduced reflectivity, at 3 $\mu$m and 6.5/7 $\mu$m corresponding to O–H stretching and H–O–H bending modes. This shows that residuals from the precursor solution are still present in Film A and that pyrolysis in case of the quartz lamps heating source was insufficient. As a consequence, the emittance $\varepsilon$, indicated in Fig. 4, is increased by about 5% with respect to the AS steel substrate. On the contrary, Film B does not show any absorption due to O–H bonds or water. Film B is totally transparent showing a reflectance similar to the AS steel substrate and thus demonstrating efficient pyrolysis during film growth by the halogen-lamp heating source. The absence of any absorption due to residuals of the precursor solution in Film B together with the XPS result of about 4% C as ZrC in Film B shows clearly that ZrC has already been formed during film growth. Furthermore, both coatings, Film A and Film B, show a strong absorption band in the UV region at 300 nm which is, in our opinion, due to Zr$^{3+}$ states in the volume of the zirconia layer, not detectable by XPS. However, we found that the coatings undergo self-curing during outdoor exposure and the Zr$^{3+}$ absorption band disappears in the reflectivity spectra (not shown). The band gap of ZrO$_2$ is about 5 eV and the corresponding band edge absorption can also be seen in Fig. 4 in both samples at about 220 nm as a steep drop in reflectivity.

Figure 5. SEM micrographs of zirconia Film A and zirconia Film B at a magnification of 1000. The black bar in each micrograph corresponds to 10 $\mu$m.
XPS depth profiles, Film A shows a much thicker coating and also a higher surface roughness. Film B, which is thinner, permits us to see also the high surface roughness of the AS steel substrate itself. No defect was found by SEM in Film B, whereas cracks were found in Film A, as can be seen in the SEM picture of Film A in the upper right section. Also regions of larger thickness, due to zirconia material accumulation, were found in both films, as can be seen, for instance, in the SEM picture of Film B at two sites where the material appears brighter. However, this did not lead to film cracks in case of Film B.

CONCLUSIONS

It has been shown that zirconia coatings of homogeneous coverage can be produced by spray pyrolysis in ambient atmosphere on large areas of aluminized steel sheets. XPS depth profiling revealed, in the case of IR radiation for substrate heating, a high C concentration in the films owing to incomplete pyrolysis and that this carbon is diluted in the zirconia film mainly as ZrC. Spectral hemispherical reflectance and SEM have shown that substrate heating with intense white light yields high-quality optical coatings; with high optical transparency, adequate absorptance and emittance for solar applications and smooth and dense surface coverage without cracks and other defects.

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