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# Large area zirconia coatings on galvanized steel sheet

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**Abstract**

Amorphous zirconia coatings have been produced by chemical spray pyrolysis on large areas of aluminized steel sheet, using the roll-to-roll technique (coil coating). SEM analysis has shown that the zirconia film is very dense without pores, covering homogeneously the steel surface of 0.4 m width (coil width). XPS and FTIR investigations revealed that no residuals from the precursor solution, in particular, water or carbon, are retained in the film. The protective character of the zirconia coating for the steel substrate has been investigated with electrochemical methods. Electrochemical corrosion experiments have shown that the corrosion resistance has been increased in saline as well as in acid conditions by more than one order of magnitude.


*Keywords:* Zr02; Thin film; Steel; Spray pyrolysis; Roll-to-roll technique; Corrosion protection

## 1. Introduction

Galvanized mild steel strips produced in coils are used in many areas of application where the steel sheet is in direct contact to the outdoor environment, for instance, in roofing and walling, automotive industry and machinery manufacturing of exterior body panels. Besides anticorrosion properties, the aesthetic finishing of large outdoor steel areas is important. An increase in corrosion resistance can be obtained by tightly adherent oxide coatings acting as physical and chemical barrier to the outdoor environment. Those oxide coatings are transparent and can have additional functionality as gloss control and interference colouring by adjusting the surface morphology and the film thickness. As large areas have to be coated, spraying in open atmosphere is an interesting and very economic option. In particular, spray pyrolysis using high pressure air as driving gas and aqueous precursor solutions has shown to be very versatile in applying different oxide coatings [1].

In previous studies we investigated systematically the spray conditions in the spray pyrolysis technique for oxide coatings applied to galvanized steel sheet, showing main and secondary effects on growth rate [2]. Also spray conditions were tuned in respect to anticorrosion properties which where evaluated by electrochemical corrosion tests in saline and acid conditions [3]. In this paper we show how zirconia coatings applied by spray pyrolysis onto aluminized steel sheet have been successfully scaled up to large area production using the roll-to-roll technique (coil coating). We comment on some results of this development from small to large area pilot production, evaluation of anticorrosion properties and analysis with respect to chemical composition and surface morphology. First results of outdoor exposure confirm an effective protection to the steel surface by the zirconia coating in comparison to the uncoated galvanized steel.

## 2. Experimental

Zirconia thin films of homogeneous coverage have been deposited in open atmosphere by chemical spray pyrolysis onto hot fired aluminized steel sheet of 0,3 mm thickness and 40 cm width with the roll-to-roll technique (coil coating; see also Fig. 1). The steel coil, in the following denominated AS, was produced at ThyssenKrupp Steel [4]. Its corrosion behavior can be found elsewhere [5]. Home-made halogen lamp reflectors of 2000 W power each were used for substrate heating and curing the film. Approx. 523 K (250 °C) and 573 K (300 °C) were used

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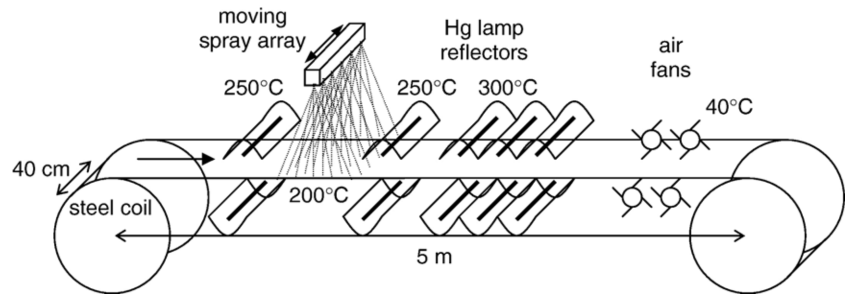


Fig. 1. Schematic drawings of the pilot roll-to-roll spray station. The steel belt moves from left to right. Processing temperatures along the steel belt are indicated.

for pyrolysis and curing, respectively. The steel sheet temperature at the different points of processing was measured with an infrared camera (TJ 200 from Tech-Jam, Tokyo) yielding thermo-pictures of 64 (8 × 8) points with an accuracy better than 1% in the temperature range from 200 °C to 500 °C. The thermal emittance of the AS steel sheet, needed as an input parameter for the infrared camera, was formerly determined from spectral hemispherical reflectance measurements with an FTIR spectrometer IFS66 from Bruker with external integrating gold sphere of 20 cm diameter [6]. Spraying was done with aqueous precursor solutions of zirconium acetyl acetonate (98% purity), in concentration $2{\cdot}10^{-2}$ M. The precursor solution consumption was 3 l per hour spraying with a spray array of 6 nozzles. The spray array was held in continuous motion by pneumatics, perpendicular to the steel belt velocity of 1.2 cm/s (see Fig. 1). The air pressure was 4 bar and the nozzle to steel belt height 50 cm. Per spray run approx. 10 nm of zirconia film was deposited. Higher film thicknesses were obtained by coiling back and repeating the spray coating process. Descriptions of different spray configurations and its comparison can be found in previous publications [1,6].

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 beam rastering of 3 × 3 $mm^2$ was assumed to be approximately 3.7 nm/min, as determined in $Ta_2O_5$ under identical sputter conditions. 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, finding that all zirconia coatings were amorphous.

Electrochemical measurements were carried out with a PGSTA 30 Autolab in 0.5 M NaCl and 0.5 M $H_2SO_4$ aqueous electrolytes. The corrosion test cell was a specially designed unit for flat large samples with three electrodes. Platinum grid

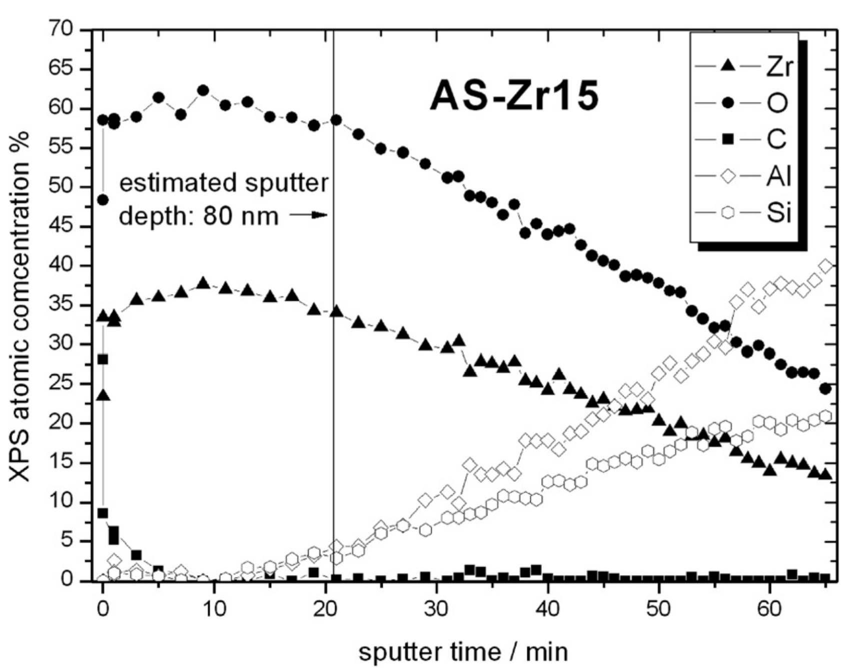


Fig. 2. XPS 4 keV $Ar^+$ sputter depth profile of zirconia roll-to-roll spray pyrolysis coated aluminized steel sheet (AS-Zr15). The sputter rate has been 3.7 nm/min. The vertical line at an estimated sputter depth of 80 nm indicates the minimum thickness of the zirconia coating Zr15 on the aluminized steel.