



Atmospheric corrosion of Galfan coatings on steel in chloride-rich environments

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ABSTRACT

Galfan coatings on steel in laboratory exposures with predeposited NaCl and cyclic wet/dry conditions exhibit nearly the same corrosion products as after 5 years of marine exposure. A general scenario for corrosion product evolution on Galfan in chloride-rich atmospheres is proposed. It includes the initial formation of ZnO, ZnAl₂O₄ and Al₂O₃ and subsequent formation of Zn₆Al₂(OH)₁₆CO₃·4H₂O, and Zn₂Al(OH)₆Cl·2H₂O and/or Zn₅Cl₂(OH)₈·H₂O. An important phase is Zn₆Al₂(OH)₁₆CO₃·4H₂O, which largely governs the reduced long-term zinc runoff from Galfan. A clear influence of microstructure could be observed on corrosion initiation in the slightly zinc-richer η-Zn phase adjacent to the β-Al phase.

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1. Introduction

Hot-dip galvanized coatings containing aluminum on steel substrates have been frequently used in automotive, construction and other industrial applications [1]. One example is the commercial Zn–Al alloy coating on steel (Zn–5 wt.% Al, trade name Galfan™, from now on called Galfan), which is commonly used in automotive applications due to its high corrosion resistance properties, superior ductility and forming properties [2]. This coating contains 5 wt.% Al, which is very close to the eutectic point (6 wt.% Al) in the Zn–Al system [3,4], and up to 0.05 wt.% mischmetal (lanthamum and cerium). The microstructure of the Galfan coating is generally characterized by a two-phase structure, a zinc-rich proeutectoid phase (<5 wt.% Al/(Al + Zn)) surrounded by an eutectic phase (5–10 wt.% Al/(Al + Zn)) consisting of beta (β) aluminum (5–25 wt.% Al) and eta (η) zinc lamellas (<5 wt.% Al) [5–8]. Since the microstructure depends on several factors such as cooling rate, annealing time and nucleation temperature in the solidification process, these factors may also influence the corrosion resistance of Galfan [9–11].

Atmospheric corrosion of zinc in natural weathering conditions has been widely investigated [12–16]. A general evolution scheme of corrosion product formation on zinc was established by Odnevall and Leygraf [17]. A thin layer of amorphous hydroxycarbonate (Hydrozincite, Zn₅(OH)₆CO₃) forms rapidly in any humid-containing atmosphere. In humid, low polluted environments, this phase

often gradually evolves into its crystalline form. If chlorides are also present in the atmosphere, zinc hydroxychloride (Simonkolleite, Zn₅(OH)₈Cl₂·H₂O) is locally formed and eventually evolves into a sodium zinc hydroxychlorosulfate (Gordaite, Na₄Zn₄SO₄(OH)₆Cl₂·6H₂O). A large number of studies have investigated the atmospheric corrosion of zinc by means of laboratory-simulated exposures [18–20]. Chen et al. studied the effect of NaCl-induced atmospheric corrosion of zinc metal by using an experimental set-up for in situ analysis, with Zn₅(OH)₈Cl₂·H₂O as the main corrosion product identified [21].

Significant knowledge exists concerning the atmospheric corrosion of zinc–aluminum coatings on steel in terms of corrosion rates and long-term corrosion product formation [16,22–25], especially for the Zn–55 wt.% Al coating Galvalume™ (from now on denoted Galvalume) on steel and for Galfan. Besides zinc-based corrosion products, Zn₆Al₂(OH)₁₆CO₃·4H₂O has been identified in several investigations [26–28] as well as Zn₂Al(OH)₆Cl·2H₂O [29]. In previous studies by some of the authors, Galvalume was investigated with respect to metal release and corrosion product evolution during short and long term atmospheric exposures [30,31]. Due to its relative simple microstructure, compared to Galfan, corrosion initiation of Galvalume was taking place in the zinc-rich interdendritic phases, whereas the aluminum-rich dendritic phases only corroded after longer exposure periods or in more severe environments [32]. Galfan has a much more complex and fine (sub-micron sized) microstructure compared with Galvalume, which may explain why very little is reported regarding its initial corrosion behavior during early stages of atmospheric corrosion and any possible correlation to its heterogeneous microstructure. Tang et al. [33] found

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that the proeutectoid η -Zn phase possesses improved corrosion resistance compared with the eutectic colonies. Yang and co-workers [34] proposed a corrosion model in which the eutectic phase was prone to preferential attack when superplastic Zn–Al alloys (4, 8, 12, 16 wt.% Al) were immersed in simulated acid rain.

This study aims to investigate the initial atmospheric corrosion mechanism and corrosion product evolution of Galfan and how this may be influenced by the microstructure. The work forms part of a larger research investigation in which one of the targets is to evaluate an accelerated corrosion test of Zn–Al coatings on steel for automotive applications, the N-VDA-test [35], from a corrosion product formation perspective. Through successive short-term controlled laboratory exposures the influence of humidity and chlorides has been elucidated by using a combination of near surface- and bulk sensitive analytical tools. Generated results have been compared with long-term data from a 5-year marine field exposure. By considering obtained corrosion product data, a general model for the evolution of corrosion products of Zn–Al coatings exposed to low-polluted humid conditions and chloride-rich environments has been proposed.

2. Materials and methods

2.1. Material and surface preparation

Non-treated Galfan (95 wt.% Zn–5 wt.% Al with additions of 0.05 wt.% cerium and lanthanum) samples were supplied from Arcelor Mittal, France. The 7 μm coating on steel was applied via a hot-dip process [2]. No mischmetal was observed in the corrosion products. The samples were cut to a dimension of 10 \times 10 mm and most samples were gently polished using a 0.25 μm diamond paste to remove the utmost high temperature oxide layer formed during the hot-dip process. Prior to the experiments, each sample was ultrasonically cleaned in analytical grade ethanol for 10 min and dried by cold nitrogen gas before stored in a desiccator overnight.

2.2. Laboratory wet/dry cycle exposure conditions and in situ surface characterization

Parallel in situ experiments were carried out by means of ESEM (environmental-scanning electron microscopy) and in situ IRAS (Infrared Reflection Absorption Spectroscopy) on Galfan samples exposed to the following cyclic exposure conditions: NaCl pre-deposition (0 or 4 μg NaCl/cm²), the first cycle 4 h (RH 90%) and 2 h (RH 0%), the second cycle 16 h (RH 90%) and 2 h (RH 0%). These cycles were repeated several times. Parallel exposures were conducted at 70% RH.

SEM imaging of surface features and IRAS spectra of corrosion product formation were generated during the dry cycles. Prior to exposure, NaCl (in a saturated 99.5% ethanol solution) was applied onto the surfaces by means of a transfer pipette. Upon ethanol evaporation, NaCl crystals were relatively homogeneously distributed over the surface. The amount of deposited NaCl was weighed by means of a microbalance (Mettler Toledo Excellence) and normalized to the geometric surface area of the samples. Detailed information of the procedure for pre-deposition of NaCl is given elsewhere [36].

Environmental scanning electron microscopy/energy dispersive X-ray analysis (ESEM/EDS) was performed using a FEI – XL 30 Series instrument, equipped with an EDAX Phoenix EDS system with an ultra-thin windows Si–Li detector. The relative humidity (RH) of the chamber was gradually increased to 70% and 90%, respectively. The acquired RH was obtained by controlling the temperature and pressure by means of a thermoelectric stage controller. Images were generated using gaseous secondary electron (GSE) detector.

To increase the resolution, images were in addition generated ex situ, switching to the normal secondary electron (SE)/backscatter electron (BSE) detector. All images (75% SE and 25% BSE) were collected using an accelerating voltage of 15 or 30 kV.

In situ infrared reflection absorption spectroscopy (IRAS) was performed in a humidity chamber on samples with and without pre-deposited NaCl. Controlled humidified conditions were obtained by mixing dry and wet pre-cleaned compressed air of reduced CO₂ (lower than 20 ppm). Experimental details are given elsewhere [37]. The IRAS spectra were recorded using a commercial Digilab 4.0 Pro FTIR spectrometer, acquiring 1024 scans with a resolution of 4 cm⁻¹ for each spectrum. The results are presented in absorbance units ($-\log(R/R_0)$), where R is the reflectance of the exposed sample surface and R_0 the reflectance of the non-exposed sample [19].

2.3. Long-term field exposure

The same batch of non-treated Galfan surfaces as investigated in the laboratory exposure were exposed at unsheltered conditions at the marine site of Brest, France for 5 years (SO₂ < 3 μg m⁻³, precipitation 800–1000 mm year⁻¹). Time-resolved measurements were conducted to assess the evolution of corrosion products (2, 4, 12, 26 and 52 weeks, 5 years). The release of zinc from the patina was determined during the 5-year period by continuously collecting and analysing the zinc concentration in the collected runoff water. All surfaces were exposed 5–10 m from the waterline at the marine site of Sainte Anne du Portzic, a cape outside the city of Brest, on the northwest coast of France. The materials were exposed at an inclination of 45° from the horizontal, facing south, according to the ISO 17752 standard for metal runoff rate measurements [38]. More detailed information of the test site is given elsewhere [39,40].

2.4. Ex situ surface characterization

A multitude of surface sensitive and non-destructive analytical methods were adopted for detailed ex situ analysis of corrosion product formation. Scanning electron microscopy and energy dispersive spectroscopy (FEG-SEM/EDS) were employed for morphological and compositional investigations, infrared (IRAS) and confocal Raman micro-spectroscopy (CRM) for information of functional surface groups and possibly their lateral distribution. Surface sensitive grazing incidence X-ray diffraction (GIXRD) was used for the detection of crystalline phases.

FEG-SEM/EDS analysis was conducted by using a LEO 1530 instrument with a Gemini column, upgraded to a Zeiss Supra 55

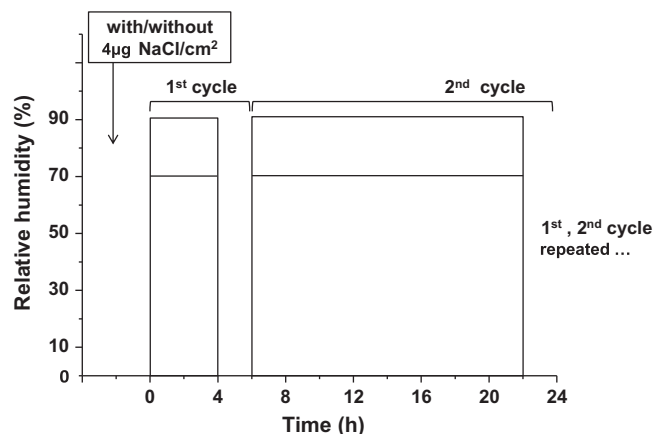


Fig. 1. Wet/dry cycle exposure conditions during laboratory exposures.

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