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Effect of surface composition and microstructure of aluminised steel on the formation of a titanium-based conversion layer

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ABSTRACT

The presented work aims at determining the influence of surface composition and microstructure of hot dip aluminium–silicon coated steel on the formation characteristics and mechanism of a titanium-based conversion layer. Varying the amount of silicon in the molten aluminium bath changes the surface nature which in turn affects the subsequent pre-treatment process. Different phases in the layer formation process were identified in the open circuit potential evolution as a function of immersion time in the conversion solution. The homogeneity and the thickness of the conversion layer in each of these regions were evaluated using secondary electron images, Auger elemental surface maps and depth profiles. While intermetallic precipitates (FeAl_3) act as nucleation centres in pure Al coatings, eutectic Si is responsible for the deposition process in a Si-rich coating. A continuous surface conversion layer is formed after 45 s of immersion in the conversion bath. Also, the presence of silicon in the coating leads to the deposition of a thicker conversion layer. A model for build-up of the conversion layer is proposed based on these observations.

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1. Introduction

The use of steel is widespread throughout several industries including transport and general engineering & construction. Often galvanised steel is used for improved corrosion protection, as the zinc coating acts as a sacrificial anode in case a defect exposes the steel to the surrounding environment [1]. However, due to volatile zinc prices, high levels of leached zinc in the environmental waters and scarcity issues, steel companies have developed alternative products like hot dip aluminium coatings on steel. Different types of aluminised steel with variable properties are commercially available [2]. In the present work two types of coatings were studied: a relatively pure aluminium coating (containing some iron) and aluminium–silicon coatings (with a variable Si content). Their good thermal resistivity leads to such coatings being used in power generation plants, exhaust systems and heating equipment [2]. Aluminium–silicon coated steel (with a high silicon content) is also investigated as an alternative for rolled electrical steel used, for example, as core metal in electrical motors [3,4].

During the aluminising hot dipping process, several parameters can be varied: dipping time, composition of the aluminium bath, cooling-down procedure, etc. All these parameters as well as the characteristics of the steel substrate have an influence on the composition and morphology of the coating [5,6]. Certain studies focused on the formation and characteristics of the interdiffusion layer that is formed at the

metal/coating interface underneath the so-called free aluminium layer [7–11]. This interdiffusion layer is a brittle intermetallic alloy compound consisting of FeAl_3 in the upper part and Fe_2Al_5 in the lower part of the layer [12]. Mechanical properties require the interdiffusion layer to be as thin as possible, which can be achieved by adding a certain amount of silicon to the molten aluminium-bath [13]. The addition of silicon also changes the composition of the sub-surface layers by the formation of Al–Fe–Si ternary compounds [14], or a eutectic silicon structure in the free aluminium layer, as was recently reported by the authors [15].

Many applications need the aluminised steel to be treated further, e.g. when a higher corrosion protection and/or a coloured finish are required. To achieve this, the metal surface is usually pretreated with a conversion layer that improves the adherence of the final organic coating. Studies of conversion processes for different aluminium alloys, have observed that the cathodic behaviour of the precipitates versus the surrounding matrix is essential for the deposition of the conversion layer. Lunder et al. [16] and Nordlien et al. [17] studied the titanium deposition mechanism on aluminium, showing that the essential processes for the film formation were the oxygen reduction and hydrogen gas evolution taking place at cathodic precipitates. These processes lead to a local pH increase at the metal surface causing the precipitation of species from the conversion solution to form a thin solid oxide conversion layer. Nordlien et al. [17] also reported that the deposition of the conversion film around the precipitates in turn reduces the cathodic activity of the precipitates and as a consequence slows down further deposition of the layer. Andreatta et al. [18] studied the influence of the precipitates in an AA6016 alloy on the (Zr/Ti)-conversion process by investigating the

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Volta potential difference between the precipitates and the surrounding aluminium matrix after different immersion times in the conversion solution. The Volta potential difference between the matrix and the precipitates was seen to decrease at the start of the conversion layer formation reaching a stable and uniform value over the entire surface when it is completely covered.

While the conversion processes of aluminium, galvanised steel and bare steel have been studied in detail, this is not the case for aluminised steel, where the complex metal surface composition and structure are expected to have a strong influence on the ongoing electrochemical reactions. This work studies the influence of the presence of silicon in an aluminium coating on a titanium based conversion layer formation process. Particular attention is paid to the influence of the silicon presence in the aluminium coatings on the time taken for the surface of the aluminium coating to be completely covered by the conversion layer and its final thickness. Finally, a model is proposed to explain the structural and compositional nature of the conversion layer.

2. Experimental

2.1. Hot dip aluminising process

The steel substrate used was a 0.8 mm thick, vapour degreased, interstitial free DC06 steel (composition indicated in Table 1) with an electron beam textured surface provided by OCAS-ArcelorMittal. The steel was aluminised on a laboratory scale using a RHESCA hot dip simulator to imitate the industrial process. During the whole dipping process a reducing N₂ (95%)–H₂ (5%) atmosphere was used to prevent the oxidation of the steel substrate during the annealing step. The sample was first heated up to 800 °C at a rate of 4 °C/s and was maintained at this temperature for 75 s. This annealing step was necessary to improve the homogeneity of the coating. Subsequently the steel was cooled down to 700 °C at a rate of 10 °C/s and was kept at this temperature for 10 s. The substrate was then dipped for 3 s in a molten aluminium bath at 660 °C. Two different types of aluminium based coatings were applied, starting from an aluminium bath containing 2 wt.% Fe and from aluminium–silicon baths containing 2 wt.% Fe and 1, 3 or 7 wt.% Si. The corresponding samples were designated as silicon-free, Si-1 wt.%, Si-3 wt.% and Si-7 wt.% respectively. 2 wt.% of iron was added to the bath to saturate it with Fe, in order to avoid the dissolution of iron from the steel into the bath that could change the bath composition when dipping a series of plates. No rinsing was applied when the sample was removed from the bath to control the coating thickness. Samples were put back in the sample chamber and cooled down to approximately 50 °C at a rate of 10 °C/s using a pure nitrogen flow (400 l/min).

2.2. The conversion treatment

Prior to the conversion treatments, all samples were ultrasonically cleaned for 10 min in ethanol. The titanium conversion stock solution used was a Granodine 1445 T solution provided by Henkel, containing dihydrogen hexafluorotitanate, phosphoric acid and organic compounds. The conversion procedure consisted of immersing the samples in a 3 wt.% Granodine 1445 T solution to which 0.250 g of ammonium nitrate per 500 ml solution was added as an accelerator. Various samples were dipped into the non-stirred solution at room temperature for 45, 105 and 300 s. The immersion of the samples was pneumatically controlled by the homemade set-up illustrated in Fig. 1. After the treatment, the

Table 1
Composition of the used steel substrate.

Fe	C	S	Ti	Mn	Si	Cr/Ni/Ci	Others
99.7%	0.003%	0.004%	0.04%	0.15%	0.02%	0.05%	Low avoidable concentrations

samples were rinsed with distilled water and dried with pressurised air. The OCP of the samples was followed during the whole conversion treatment using a Ag/AgCl reference electrode and a measuring interval of 0.1 s.

The Si-3 wt.% and Si-7 wt.% coatings had a eutectic silicon structure at the surface (see Section 3.1), which could be visualised better using an extra pretreatment step consisting of a potentiostatic polarisation at –1.6 V versus SCE during 5 min in a 1 M NaCl-solution. After the potentiostatic polarisation, the sample was rinsed with distilled water and dried using compressed air. This pretreatment exposed the eutectic structure more clearly at the surface. This was done to study the effect of the eutectic structure on the initiation of the conversion layer. Specifically, this pretreatment was only applied to study the initiation step of the conversion process with FE-SEM-EDX.

2.3. Characterisation of the samples

A Jeol JSM-7000F FE-SEM in combination with the Jeol Hyper Mini-cup EDX detector was used to characterise the surface before and after the conversion treatment. The characterisation of the surface, prior to the application of the conversion layer, consisted of identifying the intermetallics present at the surface by obtaining Backscattered Electron Images (BEI), EDX-spectra and X-ray compositional maps of Al, Fe and Si using an electron beam energy of 15 keV. After the conversion treatment, Secondary Electron Images (SEI) of the surfaces were recorded at a magnification of 5000 times and with an accelerating voltage of 10 kV. These images were combined with elemental analysis by EDX.

Additionally, Auger elemental surface maps and depth profiles were acquired after the conversion treatment with the Jeol JAMP-9500F scanning Auger microprobe. The surface maps were obtained with a primary electron beam of 10 keV and 5 nA and a resolution of 512 pixels by 512 pixels. The value used to establish the colour scale in the mapping is the {peak-background/background} intensity for each element. Prior to the acquisition of the maps, the surface was sputtered for 2 min with argon ions at a rate of around 4.3 nm/min, where the rate was calibrated on SiO₂. This step was applied to remove the surface carbon contamination.

For the elemental depth profiles, a primary electron beam of 10 keV & 5 nA and argon ion sputtering were used. The analysed area was 24 by 24 μm² and a sputter rate of 4.3 nm/min was used, calibrated on SiO₂. The sputtering time between two adjacent points of the depth profile was 30 s for conversion times of 45 and 105 s. For the conversion time of 300 s a sputter interval of 60 s was used. All Auger spectra were evaluated in the direct mode.

3. Results

3.1. The surface microstructure

The BEI of the planar surfaces of the silicon-free, Si-1 wt.% and Si-7 wt.% coatings are shown in Fig. 2. A comparison between the images, which were taken at the same magnification of 2000, clearly shows that the amount of silicon in the molten bath has an important influence on the surface structure.

At the surface of the silicon-free coating, a dense distribution of precipitates (about 2 μm in size) was observed as shown in Fig. 2(a). EDX analysis revealed that these precipitates contain approximately 27 wt.% Fe and are embedded in the pure aluminium matrix. Based on the Fe–Al phase diagram, the precipitates were identified as FeAl₃ [14]. The addition of 1 wt.% of Si to the bath, resulted in precipitates (1.5 to 3.5 μm in size) embedded in the Al-matrix (see Fig. 2(b)). EDX analysis showed that these particles contained around 30 wt.% Fe and 3 wt.% Si, corresponding to the θ-phase in the Fe–Al–Si phase diagram. These results were in good agreement with the results obtained by EBSD on cross sections of the coatings (measurements shown in [19]). When more silicon was added to the molten bath (3 wt.% and 7 wt.%)

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