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Tailoring of oxide morphology and crystallinity on advanced high-strength steel surfaces prior hot-dip galvanizing

R. Sagl [a,b,*], A. Jarosik [a], G. Angeli [a], T. Haunschmied [a], G. Hesser [b], D. Stifter [b]

[a] *voestalpine Stahl GmbH, voestalpine Straße 3, 4031 Linz, Austria*

[b] *Christian Doppler Labor für mikroskopische und spektroskopische Materialcharakterisierung, Zentrum für Oberflächen- und Nanoanalytik, Johannes Kepler Universität Linz, Altenbergerstraße 69, 4040 Linz, Austria*

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Abstract

Annealing of advanced high-strength steel (AHSS) grades often results in surfaces being fully covered by oxides due to alloying elements which diffuse to the steel surface during annealing and which are oxidized there by residual oxygen from the furnace atmosphere. However, these surface oxides tend to significantly hamper the hot-dip galvanizability and are therefore repeatedly under investigation with respect to their morphology and chemical composition for an optimization of the overall galvanizing performance. In the present work two different kinds of AHSS grades are analysed in detail by scanning electron microscopy as well as by X-ray photoelectron spectroscopy and transmission electron microscopy to characterize the formed surface oxides, clearly revealing that it is not only the chemical composition of the oxides influencing their morphology and structure: the oxidation potential of the annealing atmosphere is found to have a significant impact on the surface oxide characteristics, namely the degree of crystallinity, as well. Consequently, these findings can be used to improve the galvanizability of a steel grade by changing the surface oxide morphology.

Keywords: Steel; Crystalline oxides; Amorphous oxides; Transmission electron microscopy (TEM); X-ray photoelectron spectroscopy (XPS)

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1. Introduction

Advanced high-strength steels (AHSSs), as new materials with improved mechanical performance, require the addition of significant amounts of alloying elements to reach and adjust the desired material properties: as well as Al and Cr, Si and Mn are also essential to tune, for example, the yield strength in the desired range by the formation of different types of steel phases [1–3]. However, these alloying elements tend to diffuse to the steel surface during recrystallization annealing of the steel strip prior to hot-dip galvanizing and react there with residual oxygen being present in the annealing atmosphere, leading to the formation of oxides [4–7]. During the contact of the steel strip with liquid zinc in the zinc bath, the presence of such surface oxides on the steel strip is detrimental to its wettability [8–10], especially if the oxides are large in size or covering the steel surface like a film.

Nowadays it is state of the art to improve the hot-dip galvanizing performance by, for example, shifting the position of oxide formation from the steel surface to the steel interior [11–13]. This is achieved by increasing the dew-point of the annealing atmosphere: for an increased amount of oxygen in the atmosphere the flow of oxygen into the steel substrate exceeds the flow of oxidizable alloying elements to the steel surface [14], thereby oxidizing the alloying elements in the steel interior [15,16,4,17,18]. However, especially if there is a high amount of alloying

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* Corresponding author at: voestalpine Stahl GmbH, voestalpine Straße 3, 4031 Linz, Austria. Tel.: +43 6648 36 3771; fax: +43 50304 55 6712.
E-mail address: raffaela.sagl@voestalpine.com (R. Sagl).

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elements added to the steel grade, as is the case for most AHSSs, such an internal oxidation which leaves the surface unaffected by oxide formation is not always achievable.

To date, numerous studies have been published in the literature discussing the impact of morphology and chemical characteristics of different types of mixed oxides being present on the steel surface on the galvanizing performance of such AHSS grades. Some authors state that an accurate ratio of Si/Mn is essential to ensure a satisfying galvanizability. Suzuki et al. indicate a Si/Mn ratio of 0.33 as suitable, since the stable phases for these conditions are Mn_2SiO_4 or $MnSiO_3$ for low dewpoints and $MnO + Mn_2SiO_4$ for higher dewpoints [19], showing proper characteristics for galvanizing. According to these authors, the aim should be to avoid the formation of SiO_2, which forms in a film-like amorphous manner and hampers wetting by liquid Zn the most due to the large lateral extension of the oxide films. This effect would especially occur for a ratio of Si/Mn > 1, where the formation of SiO_2 is expected to be unavoidable regardless the oxidation potential. For a dewpoint higher than −5 °C, SiO_2 would also not form for a ratio of Si/Mn = 1. However, as the dewpoint in standard annealing conditions on an industrial hot-dip galvanizing line is in the range of −25 °C to −10 °C, the formation of SiO_2 can thus only be prevented for a ratio of Si/Mn < 0.5, where $MnSiO_3$ and Mn_2SiO_4 would be the stable phases [19].

Furthermore, oxidation often seems to happen in a "discontinuous" manner [20]. Ollivier-Leduc et al. report that Mn oxides in the state of MnO form at 650 °C, but change into a mixed state together with Si at higher temperature, forming Mn silicates or Mn–Si mixed oxides [5]. According to that, Van de Putte et al. state that MnO starts to appear at 500 °C, but is transformed to Mn_2SiO_4 via the reduction of MnO with SiO_2 [21]. In contrast, Drillet et al. report that Mn_2SiO_4 grows on top of an amorphous SiO_2 layer, which is assumed to be the first growing phase [22]. In an earlier work, Van de Putte et al. describe that at a temperature of 650 °C the first growing oxide has a higher Mn concentration, whereas for higher temperatures diffusion of Si becomes more pronounced. Finally, at a temperature higher than 850 °C, Mn_2SiO_4 starts to grow [23]. A different observation is reported by Gong et al., who describe lens-shaped particles consisting of amorphous SiO_2 with MnO in solution [24]. Regarding the crystallinity of Si–Mn mixed oxides, some authors assume that the Mn content in the oxide is responsible for the characteristics. Gong et al. describe, for example, crystalline oxides with the stoichiometry of $x\mathrm{MnO}\cdot\mathrm{SiO_2}$ ($x \geqslant 2$) and amorphous oxides with a stoichiometry of $x\mathrm{MnO}\cdot\mathrm{SiO_2}$ ($x < 0.9$) [23].

All of the above-mentioned studies agree in the point that the composition as well as the ratio of the alloying elements (Si/Mn ratio) and the resulting chemical composition of the oxides are the most critical factors for the final galvanizing performance. However, in this present study it is shown for the first time that the oxidation potential of the annealing atmosphere not only has a significant impact on oxide formation – by leading to an internal oxidation of the alloying elements for high dewpoints – but is also an essential factor to increase the crystallinity of the surface oxides, although the overall concentration of the oxidized alloying elements on the steel surface is kept constant with increasing dewpoint.

For these investigations, two different kind of steel grades with different Si, Mn and Al contents were annealed at various oxidation potentials (dewpoints). Advanced analysis techniques like X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) were implemented besides scanning electron microscopy (SEM), to characterize the surface oxides formed by annealing at low dewpoints (low oxidation potentials) as well as for a higher ones (high oxidation potentials). By comparing these results, it is indicated that not only the chemical composition of the oxides, but also the oxidation potential of the annealing atmosphere itself, influences the oxide characteristics and structure in a way leading to a potentially improved galvanizability.

2. Material and methods

2.1. Sample preparation

The Mn, Si and Al contents as well as the Si/Mn ratios of the steel grades investigated are given in Table 1. Alloy 1 exhibits Mn and Si contents quite typical for a transformation-induced plasticity (TRIP) bainitic ferrite (TBF) steel grade. With these contents the Si/Mn ratio for alloy 1 is set to 0.33, which is assumed to be the proper ratio resulting in a good galvanizing performance [5]. The chemical composition of alloy 2 is typical for a TRIP steel grade, showing a lower Si/Mn ratio but a high Al content.

For the investigations, the cold-rolled samples were cleaned in an alkaline solution at 70 °C to remove any residual contaminants of, for example, oil. The cleaned samples were annealed and hot-dip-galvanized in a galvanizing simulator at voestalpine ("GalvaSim"). For the adjustment of a standard annealing atmosphere, a N_2–5% H_2 atmosphere was used with varying amounts of H_2O to reach the desired dewpoint and therefore oxidation potential. The samples were heated to 800 °C with a heating rate of 25 K s^{-1} in an infrared furnace and held at that temperature for 60 s. After soaking, the samples were cooled with a cooling rate of ~25 K s^{-1} to a temperature of 460 °C and hot-dipped in a Fe-saturated zinc bath containing 0.20 wt.% Al for 3 s. After hot-dipping, the samples were cooled to room temperature. For the fabrication of only annealed but not galvanized samples, cooling was

Table 1
Mn and Si contents of the three alloys investigated.

Alloy name	Steel grade	Mn	Si	Al	Si/Mn ratio
Alloy 1	TBF steel grade	2.5	0.8	0.6	0.32
Alloy 2	TRIP 700	1.8	0.3	1.0	0.17