ABSTRACT

The steel surface condition after continuous annealing is extremely important to the quality of galvannealed coating (GA). The presence of oxides can affect the reactions at the coating/substrate interface and decrease the zinc wettability on the steel surface. To avoid oxidation, a protective atmosphere is used during the annealing. Despite this, it is possible the selective oxidation occurs and dew point is one of the leading factors in order to obtain a favorable surface to galvanizing. This study evaluated the effect of dew point on the quality of GA coatings applied to bake hardening steel. Continuous annealing under dew points from -60°C to 0°C, as well as galvanizing, was performed in a Hot Dip Process Simulator (HDPS). It was found that the dew point has a decisive influence on the amount, distribution and type of formed oxides, and the condition of -30°C provided the coatings with better quality.

KEYWORDS

Continuous annealing, dew point, selective oxidation, bake hardening steel, galvannealed coating

INTRODUCTION

The hot-dip galvanized (HDG) steels have been extensively used in the automotive industry due to their excellent corrosion resistance, good weldability and formability. These characteristics are especially shown by the GA-coated steels produced in continuous galvanizing lines (CGL) with coating heat treatment. This coating is formed by a mixture of different intermetallic Fe-Zn phases.

The surface condition of the steel after annealing is of utmost importance for the quality of HDG coatings. The presence of oxides, precipitates, oily residues and/or exogenous particles in the process can affect the reactions in coating/substrate interface. Their presence can also affect the wettability of the steel surface by the liquid zinc, resulting in possible defects in the final product.

A slightly reducing atmosphere (typically mixture of H₂ and N₂) is employed during the annealing furnace to avoid the surface oxidation, as well as the oxides presence on the surface steel. However, the selective oxidation of elements such as Al, B, Si, Mn, Ti, and P, in addition to Fe, is possible to occur during the annealing of the strip. Especially, the high alloy steels have highly susceptibility to these phenomena. The present moisture in the protective atmosphere of the annealing furnace is one of the most important factors to be considered to mitigate this occurrence. The effect of the selective oxidation during the annealing is the formation of defects such as lack of coating or poor coating surface quality.
In this context, the effect of the dew point (DP) of the annealing furnace atmosphere in the quality of the GA coating applied on a bake hardening (BH) steel was studied. It was identified the relationship between the oxides formed on the substrate surface and the characteristics of the coating obtained.

EXPERIMENTAL METHOD

A cold rolled BH steel with yield strength of 210MPa (BH210) and thickness of 0.7mm was evaluated in this study. Its composition is shown in Table 1.

| Table 1 Composition of the BH210 steel (wt%) |
|-----|-----|-----|-----|-----|-----|
| C   | Mn  | Si  | P   | Al  | B   |
| 0.0015 | 0.60 | 0.007 | 0.045 | 0.050 | 0.0012 |

In a first step, samples of cold rolled steel were annealed in HDPS under protective atmosphere of 95% N₂ + 5% H₂. The heat treatment was performed with DP values of -60°C, -30°C and 0°C. The quantity of formed oxides on the steel surface during annealing, as well as its distribution in the surface and subsurface regions were analyzed by: (i) X-ray photoelectron spectroscopy (XPS) using a monochromatic X-ray source of Al Kα. Prior to this analysis, the surface of the samples was cleaned by sputtering with 2keV/1uA, during 30 minutes. The background of the spectra were subtracted using a Gaussian-Lorentzian function; (ii) Field-emission gun scanning electron microscopy (FEG-SEM) using images of secondary electrons (SE); and (iii) Glow discharge optical emission spectroscopy (GDOES).

In a second step, the effect of the oxides on the GA coating quality was evaluated by: (i) values of Fe and Al content measured by inductively coupled plasma optical emission spectrometry (ICP-OES) and (ii) SEM images using SE of surface and cross section morphology.

RESULTS AND DISCUSSION

According to XPS analysis, Mn was the most abundant element on the surface of BH210 steel for all dew points evaluated and it was identified by the peaks in Mn2p level. The results of quantitative analysis of this element are shown in Fig. 1. These results show that as drier the annealing atmosphere, was greater the Mn diffusion to the BH210 steel surface, which is in accordance with Wagner's theory for internal/external selective oxidation [1], since at higher dew points the amount of available oxygen in the atmosphere is greater, resulting in higher concentrations of this element inside the steel and, consequently, its internal oxidation. After deconvolution and indexing of the Mn2p3/2 peaks, it was found that, except at the dew point of -30°C, Mn was on the BH210 steel surface as simple oxides (MnO or Mn₃O₄) [2-8], as well as mixed oxides with other elements [5,7,8]. For the annealed sample with dew point of -60°C there was the largest amount of Mn in the form of mixed oxides. For wetter atmospheres, although Mn was lower in surface concentration, mixed oxides were also formed.
The distributions of Mn along the thickness were investigated by GDOES and are shown in Fig. 2. According to XPS results, as drier the atmosphere was greater the Mn enrichment on the BH210 steel surface. At high dew points, Mn diffusion to the surface is low, allowing more intense oxidation of this element in the internal regions (approximately 0.06 µm from the surface). These observations, as well as those obtained via XPS are in agreement with Eynde et al. [4], whose found that the external oxidation of Mn is disadvantaged at high dew points.

The XPS analysis identified the peaks listed in Table 2 for the elements present in small concentration, with their respective binding energies (BE) and surface concentrations.
Table 2  XPS peaks identified on the BH210 steel surface annealed under different dew points

<table>
<thead>
<tr>
<th>Element</th>
<th>BE</th>
<th>wt%</th>
<th>Indexing</th>
<th>-60°C</th>
<th>-30°C</th>
<th>0°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (level Si2p)</td>
<td>102.18 eV</td>
<td>1.7%</td>
<td>Mn₂SiO₄ or MnSiO₃</td>
<td>Unidentified</td>
<td>103.81 eV</td>
<td></td>
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<td></td>
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<tr>
<td>P (level P2p)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>134.06 eV</td>
<td>4.7%</td>
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<td></td>
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<td></td>
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<tr>
<td>Al (level Al2s)</td>
<td></td>
<td></td>
<td>Al₂O₃</td>
<td></td>
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<td></td>
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<tr>
<td>B (level B1s)</td>
<td></td>
<td></td>
<td>B₂O₃</td>
<td></td>
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<tr>
<td>Ti (level Ti2p)</td>
<td></td>
<td></td>
<td>TiO₂</td>
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</tr>
</tbody>
</table>

The Si peaks in the level Si2p were identified on the surface of the samples annealed with dew points of -60°C and 0°C, with greater intensity in the humid atmosphere. Eynde et al. [4] also found higher Si oxidation at high DP values. The peak identified in the annealed sample with DP of -60°C was associated with the mixed oxides of Mn and Si (Mn₂SiO₄ or MnSiO₃) [4,8]. On the other hand, the Si2p peak identified for the DP of 0°C corresponds to SiO₂ [4,5,8,10]. Parezanović [9] observed that oxides mixed with Mn have low wettability by Zn and Blumenau et al. [11] identified that the wettability of Zn is also highly degraded by SiO₂ on the steel surface.

By XPS, P was detected only for DP of 0°C. Swaminathan et al. [8] and Liu et al. [12] proposed this peak corresponds to Mn₃(PO₄)₂. Guttmann et al. [13] found that surface enrichment of P at some steel hardened by solid solution increases significantly after annealing in humid atmospheres. The distributions of P along the thickness from the surface are in Fig. 3.

![Fig. 3  P concentration profiles by GDOES to BH210 steel annealed under different dew points](image-url)
In accordance to XPS analysis, the results shown in Fig. 3 indicated the P concentration on the BH210 steel surface was higher when the material was annealed under the high DP (0°C). The external oxidation of P was disadvantaged in dry atmospheres.

Al was identified on BH210 steel surface only after annealing under dew point of -60°C, through a peak at the Al2s level indexed as Al2O3 [14].

Peaks at level B1s were identified on the annealed steel surface under -60°C and 0°C dew points, which can be indexed as B2O3 [5].

The peaks identified at Ti2p level in the annealed samples at -60°C and 0°C dew points suggested the presence of TiO2 on the BH210 steel surface [15].

Fig. 4 shows the surface morphology of samples annealed under the evaluated dew points. The formed oxides on BH210 steel surface annealed under DP of 0°C were globular or ellipsoid with high incidence on grain boundaries and low density within the grain. The morphology and distribution of oxides on the steel surface annealed under DP of -30°C differed significantly from those observed for the wetter atmosphere. In this case, the oxides had different polygonal shapes and sizes. Few globular particles were observed inside the grains, whose boundaries were filled with small oxides. After annealing under the DP of -60°C, the steel surface presented oxides of various shapes (polygonal, globular and stick) and sizes. The grains had a medium oxides density and the grain boundaries were partially filled with different shapes and sizes oxides.

The concentrations of Mn, Si, P, Al, B and Ti obtained by XPS at the surface of samples annealed under different DPs, as well as the sum of the percentages of all these alloying elements are shown in Fig. 5. According to these results, DP was determinant for the amount and type of oxides formed on BH210 steel surface. At -60°C dew point, a high diversity and total percentage of oxides were formed. For the DP of -30°C, despite the considerable amount of oxides, only Mn oxides formed on the surface. On the other hand, the amount of oxides formed was small in the wet atmospheres, due to the low Mn content that migrated to the surface, despite their great diversity.
Fig. 5  Elements concentrations by XPS on the steel surface annealed under different dew points

The BH210 steel appearances coated after the continuous annealing under the different dew points are shown in Fig. 6. It can be seen that the most homogeneous appearance was presented by GA coating obtained under the DP of -30°C.

Fig. 6  Appearance of samples coated after the continuous annealing under different dew points

The amount of Fe and Al content in GA coatings applied to BH210 steel are shown in Fig. 7 for the evaluated dew points. The Al content variation with the dew point employed was irrelevant, since all coatings presented Al contents typical for industrial GA products. On the other hand, there was a tendency to increase the Fe content of GA coating with the increase of dew point during the continuous annealing.
The difference of the morphology of the GA coatings is shown in the Fig. 8. The coatings became more homogeneous and refined with the DP increase, indicating more orderly phase transformation during its heat treatment. This great homogeneity may be explained by the high surface reactivity of steel annealed under wetter atmospheres, as a result of few oxidized surface alloying elements. On the other hand, as dew point decreased, the coating morphology became more heterogeneous, with low relief regions, typical of more disordered Fe-Zn phase transformation during the galvannealing treatment. As the protective atmosphere became drier, the greater amount of oxides on the BH210 steel surface limited Fe diffusion to the formation of Fe-Zn phases, producing coatings of more heterogeneous morphology. This result is in agreement with those obtained for Fe content in GA coatings, Fig. 7.

Fig. 9 shows the cross sections of GA coatings in regions with large failures. These results confirm further deterioration of GA coatings applied to steel annealed under DP = 0°C. The cross section of the coating obtained with a DP of -30°C was free of defects, which may be justified by the formation of only simple oxides of Mn (MnO or Mn₃O₄), since the wettability of these oxides by liquid Zn is reasonably satisfactory [9]. On the other hand, for DP = -60°C the cross section of the coating showed a slight deterioration. It should be noted that under this condition of dry protective atmosphere, there was a high external oxidation of Mn. This external oxidation occurred in addition to the considerable formation of mixed oxides of Mn and other alloying elements, which have low wettability by liquid Zn [9]. Finally, at the dew point of 0°C, the formation of mixed oxide Mn₃(PO₄)₂ and SiO₂, whose wettability by liquid Zn is unsatisfactory [9,11], deteriorated the quality of the GA coating.
Fig. 9 Cross section of GA coatings applied on samples annealed under different dew points

CONCLUSION

The coating applied on BH210 steel annealed under dew point of -30°C showed the best surface quality since the oxides formed (MnO or Mn$_3$O$_4$) have satisfactory wettability by liquid Zn, despite the intense external oxidation of Mn. In the driest atmosphere (-60°C), the quality of the coating was compromised due to high occurrence of Mn external oxidation, allied to the fact that the mixed oxides formed under these conditions (Mn$_2$SiO$_4$ or MnSiO$_3$). These formed oxides have low wettability by liquid Zn. Under the dew point of 0°C, the coating showed the worst quality due to selective oxidation of P, forming mixed oxide with Mn (Mn$_3$(PO$_4$)$_2$), despite the lower Mn external oxidation. In addition, the formation of SiO$_2$ was noticed, which have unsatisfactory wettability by liquid Zn. The dew point also influenced the morphology of the GA coating. Under a dry atmosphere, the predominance of external oxidation in BH210 steel limited the Fe diffusion for Fe-Zn phase formation during galvannealing treatment, producing heterogeneous coating and higher crystal refinement.

REFERENCES