

Influence of Selective Oxidation Phenomena in CGLs on Galvanized Coating Defects Formation

Y. F. Gong, S. Biroasca, Han S. Kim, and B. C. De Cooman[†]

*Materials Design Laboratory, Graduate Institute of Ferrous Technology
Pohang University of Science and Technology, Pohang, Korea*

The gas atmosphere in continuous annealing and galvanizing lines alters both composition and microstructure of the surface and sub-surface of sheet steel. The formation and morphology of the oxides of alloying elements in High Strength Interstitial Free (HS-IF), Dual Phase (DP) and Transformation-Induced Plasticity (TRIP) steels are strongly influenced by the furnace dew point, and the presence of specific oxide may result in surface defects and bare areas on galvanized sheet products. The present contribution reviews the progress made recently in understanding the selective formation of surface and subsurface oxides during annealing in hot dip galvanizing and conventional continuous annealing lines. It is believed that the surface and sub-surface composition and microstructure have a pronounced influence on galvanized sheet product surface quality. In the present study, it is shown that the understanding of the relevant phenomena requires a combination of precise laboratory-scale simulations of the relevant technological processes and the use of advanced surface analytical tools.

Keywords : *galvanizing, galvannealing, TRIP, HS IF, oxidation*

1. Introduction

The enhanced passengers' safety, better crash-resistance and lighter car body weight are being given more consideration in the automotive industry nowadays. Steel is the main material for car bodies, and formable high strength steels have been developed to meet the safety requirements these days. Meanwhile, the use of high strength steels in the automotive industry will also increase the fuel efficiency and reduce the cost of manufacturing car bodies.^{1,2)} However, the use of high strength steels in automotive industry greatly relies on the corrosion resistance and durability of thin gauge DP or TRIP steel. The Zn coatibility of high strength steel is an important factor to guarantee the application of new high strength steels in a car body. Therefore, the continuous galvanizability of Dual Phase (DP) and TRIP steels is essential for determining the application of thin gauge DP or TRIP steel. TRIP steel poses a significant challenge to be galvanized directly in current continuous hot dipping or electro-plating lines. Although many automotive lines have tested the hot dip galvanizing behavior of High-Strength Interstitial Free (HI-IF) and Dual Phase (DP) steels, few solutions are available for

the galvanization of TRIP steels in practice.

The current products for cold rolled HS-IF, DP, Complex Phase (CP), and TRIP steels require high amounts of Mn, Si, P and Cr, and small amount of Mo is also preferable in some cases.^{3,4)} The alloying elements in Advanced High Strength Steels (AHSS) may segregate on the sheet surface and oxidize in the atmosphere of the current annealing process after cold rolling. In case of TRIP steels, the processing conditions must be strictly controlled at the soaking temperature in order to sustain a specific phase fraction. This requires different soaking temperatures and transformations from those of low carbon steels. However, the techniques of Hot Dip Galvanizing (HDG) lines are seldom optimized for TRIP steels. The element segregations on the surface of sheet steels have been observed in high vacuum conditions,⁵⁻⁷⁾ and they occur in the form of oxides in the continuous annealing conditions.⁸⁾ The surface morphology and surface distributions of segregates significantly influence the wetting and the reactivity towards liquid Zn, which also have considerable effects on the formation of $\text{Fe}_2\text{Al}_{5-x}\text{Zn}_{5x}$ inhibition layer and the strength of the coating adhesion in the galvanizing (GI) line.⁹⁾ It is believed that the formation of a dense, continuous and strongly adherent $\text{Fe}_2\text{Al}_{5-x}\text{Zn}_{5x}$ layer on the TRIP steel surface during the galvanized (GI) coating is extremely im-

[†] Corresponding author: decooman@postech.ac.kr

portant.

The original surface of the steel which was produced in continuous annealing processes influences the surface quality of galvanized (GI) and galvanized (GA) coatings to a great extent.^{10,11)} The steel surface reacts with the Zn bath and the coating layer solidifies on the inhibition layer. The original steel subsurface becomes a part of Zn/Steel interface. Therefore, imaging and analyzing the original steel surface conditions will be extremely difficult, particularly when trying to identify the surface defects. However, recent modern surface analytical techniques make it possible to understand the fundamental role of the surface and subsurface oxidation state on the formation of the galvanized coating defects.¹²⁾

2. Mechanism of the surface and subsurface selective oxidation and the surface defects formation in continuous galvanizing lines

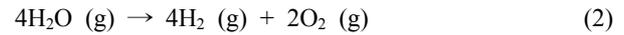
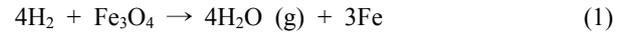
The understanding of the surface and subsurface phenomena of galvanized products is essential to clarify the effect of elements oxide formation on the galvanized products surface quality. The formation of the surface defects is closely related to the oxidation characteristics, *i.e.*, wettability. These will be discussed in the following two paragraphs.

2.1 Formation of surface and subsurface selective oxides

Although the protective atmosphere during the recrystallization annealing in the continuous hot dip galvanizing or galvannealing process reduces the Fe oxides and leads to the formation of pure Fe surface, the alloying elements with higher affinity for oxygen such as the ubiquitous Mn and Si may find preferable nucleation sites on the surface. Selective oxidation, which might develop externally on the steel surface or internally below the free steel surface, depends on the dew point of the furnace atmosphere, the susceptibility of alloying element to oxidation and the oxide solubility. Furthermore, the type of oxidation is dominated by the diffusion of oxygen and metallic elements. If the diffusion of metallic element is dominant, the oxygen will react with the alloying elements on the surface and result in the formation of an external oxide. Alternatively, the oxygen will diffuse into the subsurface region, where it forms an oxide particle with alloying elements if the solubility product of oxide is reached locally.^{12),13)}

The oxygen in the furnace atmosphere is provided the reduction of the Fe-oxides by H₂ and it forms at a low temperature during the heating stage of the crystallization cycle. The dissociation of the water vapor thus forms on

the surface of the steel according to the following reaction scheme (Eq. 1, Eq. 2, Eq. 3):



O₂ (g), (O₂)_{abs} and [O]_{diss} are the oxygen in the atmosphere, absorbed on the free iron surface and dissolved in the iron matrix, separately. Practically, the dew point can be increased by passing the part of the furnace gas flow through a humidifier. This provides an extra amount of H₂O which results in an extra amount of [O]_{diss}.

The oxygen in the atmosphere depends on the fraction of the oxygen adsorbed (O₂)_{abs} on the free surface, which is in return dependant on the oxygen partial pressure p_{O2}. With the increase in the dew point, more oxygen diffuses into the steel. Once the solubility limit of a particular oxide is reached, it causes the internal oxide formation. The oxygen solubility, the content of alloying element X and the diffusivities of both O and X, determine the transition from external to internal oxidation in simple binary Fe-X alloys. In multi-phase microstructures such as the one present at the surface of TRIP steels in the intercritical range, the surface state may become difficult to predict, especially when the properties are phase-dependant.¹³⁾ Moreover, the formation of complex oxides must be considered as well.

The general principles of the oxide formation are well understood. At the low oxygen partial pressure, p_{O2}, there is no formation of Fe-oxides, but alloying elements are generally selectively oxidized.¹⁴⁾ At low dew points, the oxidation layer is extremely shallow in general typically of a few tenths of a micron and the surface oxidation is prevalent (Fig. 1). This situation is clear for Mn, Si, Al, Cr and Ti in most continuous annealing furnaces where the p_{O2} is set by the amount of hydrogen and the dew point of the N₂-H₂ gas. The enrichment of alloying elements with oxidization may lead to the poor wetting characteristics of the steel surface in liquid Zn. On the other hand, high values of p_{O2} tend to lead the formation of internal oxides as the alloying elements form subsurface oxides. The oxidation front is within a few microns below the surface and the oxides are present internally (Fig. 1). An extension of the original Wagner theory was used to model the mechanism of the internal oxidation under conditions relevant to the industrial practice.¹⁵⁾⁻¹⁹⁾ The most important features of current models for selective internal oxidation are illustrated in the schematics of Fig. 1.

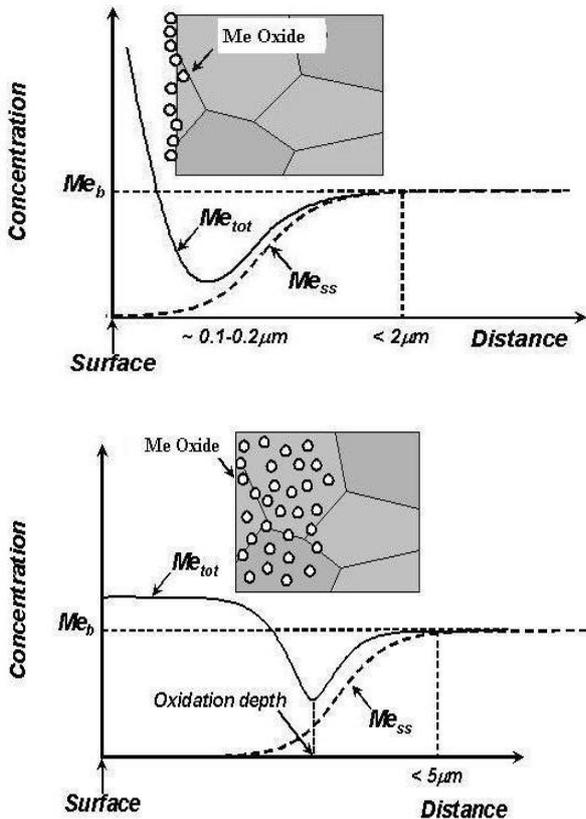


Fig. 1. Mechanisms of selective oxidation in atmosphere at low (right) and high dew point (left). Me_{tot} and Me_{ss} are the total content of the alloying element and content in solid solution respectively.

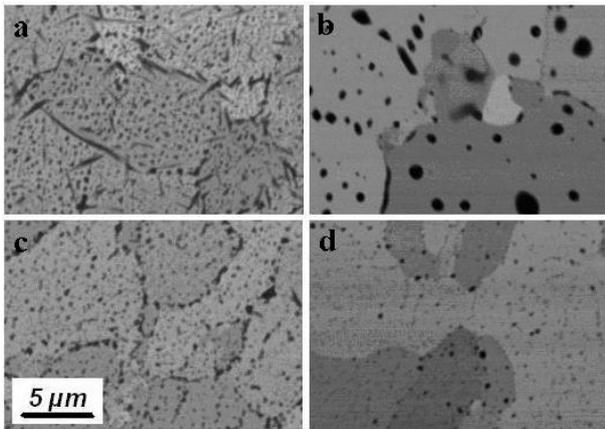


Fig. 2. SEM micrographs of the surface of a TiNb IF steel (Composition (wt%): a and c: 0.072% P, 0.98% Mn; b and d: 0.084% P, 0.11% Mn), Dew point: (a and b: -30°C ; c and d: -10°C).

Although the experimental verification of the internal oxidation models for Fe-Mn and Fe-Si alloys has been carried out,²⁰⁾⁻²³⁾ the interaction among several elements

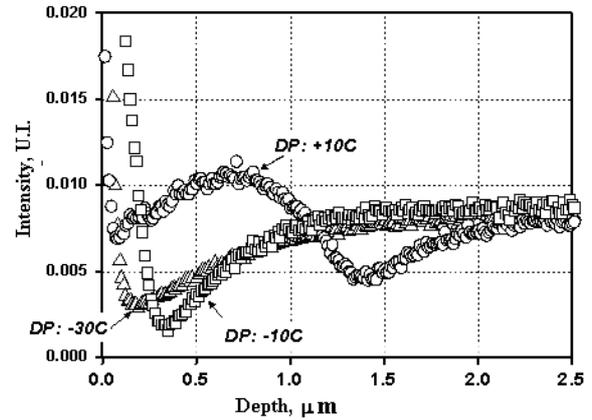


Fig. 3. GDOES depth profiles of TiNb IF steel after annealing in a $\text{N}_2\text{-}5\%\text{H}_2$ gas mixture with a dew point of -30°C , -10°C and $+10^{\circ}\text{C}$.

for the more complex multi-element Fe alloys is extremely difficult, particularly for complex oxide compounds. Fig. 2 illustrates the evolution of the selective oxidation of Mn at the TiNb IF steel surface showing the influence of the dew point of the annealing $\text{N}_2\text{+}(5\%)\text{H}_2$ atmosphere and the Mn content changes. The particles with a black contrast are MnO. The analysis of the same material by using Glow Discharge Optical Emission Spectrometry (GDOES) is shown in Fig. 3. It is observed that the Mn-oxidation front gradually moves inward as the dew point is increased. The Mn-oxidation front is near the surface of the steel when it was annealed in a low dew point atmosphere. The Mn concentration profile has a characteristic subsurface oxidation “hump” from 0.5 to 1 μm below the surface in the case of high dew point, in other words, in the case of internal oxidation conditions.

2.2 Mechanism of surface defect formation related with oxidation in continuous galvanizing line

The surface conditions of steel strip prior to entering Zn bath in a Continuous Galvanizing Line (CGL) is of prime importance for controlling the wetting of the steel surface by liquid Zn. Both the steel surface state and the immersion processes in liquid Zn determine the eventual coating qualities. It is clear that the only characterization of the steel sheet surface prior to dipping is unable to predict all interfacial processes occurring in the liquid Zn. Small external oxide particles may cause little or no coating quality problems because the dissolution of the surrounding steel can lead to their exfoliation or their incorporation in the inhibition layer or Zn-Coating. Fig. 4 shows the analysis of the inhibition layer on TiNb IF-steel alloyed with Mn and P using electron microscopy. The inhibition layer acts as an extraction replica for compound

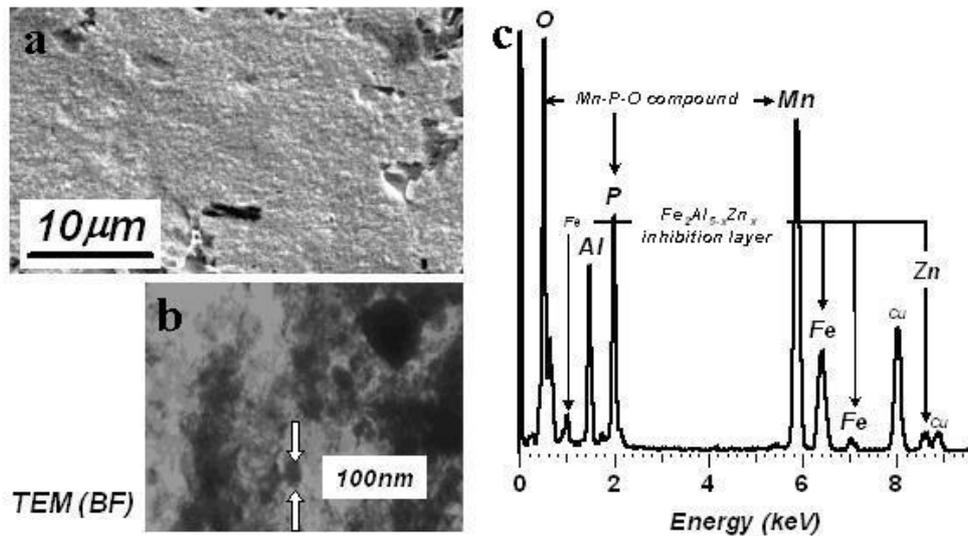


Fig. 4. SEM (a) and TEM (b) analysis of the inhibition layer formed on a TiNb IF steel alloyed with Mn and P. SEM micrograph (a) and EDS(c) shows that the inhibition layer forms a continuous film.

oxides of Mn and P present on the steel surface or in the sub-surface region. The SEM micrograph (Fig. 4a, c) shows that the oxide is probably the Mn-P-O compound product. Fine oxide particles containing Mn and P with the size of 10 nm are imbedded in the inhibition layer (Fig. 4b). However, their presence did not prevent the homogenous inhibition layer formation. No coating defects were observed on the galvanized panels for this type of IF steel. On the other hand, the adherent film-like surface oxides may significantly hinder the inhibition layer formation by preventing the dissolution of Fe in the liquid Zn, meanwhile, they may also prevent the wetting of the steel surface in liquid Zn due to the surface tension effects. Fig. 5 shows the case occurring in the conventional CMnSi TRIP steel with high Si. Despite the fact that the traditional CMnSi

TRIP steel can not be galvanized conventionally, the wettability of the conventional CMnSi TRIP steel panels in the liquid Zn can be improved significantly through the substitution of Si by Al, see Fig. 5. A high-quality coating without any noticeable bare or other galvanizing-related defects is obtained when Si is fully replaced by Al. As shown in Fig. 5, the increase in the annealing atmosphere dew point can improve the galvanizability of CMnSi TRIP steel. Although the Zn coating covers the entire steel surface under high dew point conditions in contrast to the low dew point condition, some small bare areas are still present. Nevertheless, the coating quality of CMnSi steel remained inferior to the coating quality obtained for the CMnAl TRIP steel. This indicates that the combination of Si and Mn results in the formation

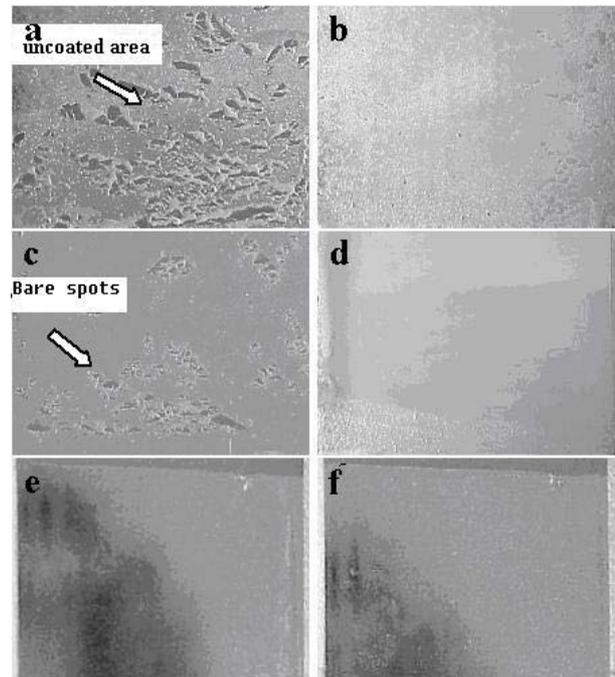


Fig. 5. Typical visual appearance of the surface defects on as-galvanized CMnSi (a, b), CMnAlSi (c, d), and CMnAl (e, f) TRIP steel. Dew points during annealing were low (left: a, c, e) and high (right: b, d, f).

of the film-like SiO_2 and Mn_2SiO_4 oxides that cause the poor galvanizing properties in the case of CMnSi TRIP steel (Fig. 5a, 5b). This was quite evident in the case of the annealing in the low dew point atmosphere where no Zn coating was obtained, see Fig. 5a. In contrast, the pres-

ence of external MnO, MnO₂, FeAl₂O₄ and MnAl₂O₄ oxides did not deteriorate the galvanizability of the CMnAlSi and CMnAl TRIP steel strip (Fig. 5c, 5d, 5e, 5f). It is believed that a similar situation occurs in the Si alloyed TiNb IF steel and that even relatively small amounts of Si can result in the presence of bare spots and other coating defects in the Zn layer.¹²⁾

3. Conclusions

An understanding of the oxidation phenomena on steel surfaces and subsurface during annealing in a hot dip galvanizing and conventional continuous annealing line needs further experimental considerations. The increasing interest in this subject must come from the realization that the surface and subsurface composition and microstructure critically influence the sheet product quality of galvanized steels. The presence of specific surface oxides may actually cause many coating defects. Therefore, there are many interesting topics to be tackled for the future research of steel strips:

Applied Surface Science: The steel strip surface obtained in the industrial continuous HDG lines is not available for the direct analysis. A laboratory simulator with the flexible thermal cycles and precise gas atmosphere control needs to be designed. In addition, the laboratory simulator also needs to be integrated with advanced *in situ* surface analysis equipments. The high resolution TEM and Focused Ion Beam (FIB) technology for the preparation of the specimen have to be employed in order to get the better resolution characterization of the oxides.

Process development: The annealing furnace technologies should adopt the flexibility in the control of the gas atmosphere in HGD lines, especially in the flexible control of the dew point.

Modeling: Models for ternary and multi-element ferrous alloys need to receive much more attention in spite of some better understanding of the binary system Fe-Mn and Fe-Si. The effect of interactions between different elements and the formation of complex rather than simple oxides in multi-element alloys will have to be addressed in particular. The multiphase surfaces need to be studied in order to understand the specific coating behavior of GI and GA processes on advanced high strength multiphase steel.

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