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The origin of striations on the surface of iron–zinc coated steel sheet produced by hot-dip galvannealing

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Dark striations are often observed on the surface of iron–zinc coated steel sheet annealed immediately after hot-dip galvanizing (galvanneal). The striations can be explained on the basis of the differential formation of an iron–aluminium barrier layer at the steel-bath interface during galvanizing. The contact of a submerged, grooved sink roll in the galvanizing bath with the steel sheet causes variations in the iron–aluminium barrier layer at the interface. A more coherent layer is formed in the areas where there is no contact *i.e.*, the grooved areas on the sink roll. The growth of the iron–zinc coating under a higher local aluminium concentration during subsequent annealing leads to a pitted surface in those groove areas, and creates the appearance of dark striations on the surface of the coated sheet. The aluminium content of the galvanizing bath is a key factor in determining the extent of the non-uniformity imposed by the contact with the sink roll. Consequently the striations can be reduced by lowering the aluminium content of the galvanizing bath.

1. Introduction

The manufacture of hot-dip galvannealed steel involves the passage of steel sheet through a molten galvanizing bath to coat the sheet with zinc, and immediately annealing it to form an iron–zinc interdiffusion coating [1]. The passage of the steel strip through the molten galvanizing bath is achieved with a submerged roll, or ‘sink roll’ within the galvanizing bath, around which the steel strip is passed to permit contact with the melt [2]. Fig. 1 shows a schematic view of such an arrangement. The sink roll is usually made of a material resistant to attack by molten zinc and is often coated with wear resistant coatings. Circumferential grooves are often machined on the surface of the sink roll for better hydrodynamic performance when the roll is rotating in the galvanizing bath. During the passage of the steel strip through the bath, one side is in contact with the sink roll for a portion of the time that it is submerged in the melt. This contact with the roll could affect the galvanizing reactions that occur in the bath under certain conditions and hence affect the subsequent interdiffusion of iron and zinc. When the surface of the sink roll is worn, or marred in some manner, or if extraneous particles (dross) are imprinted on the surface, there is a transfer of the surface characteristics to the steel strip which affects the appearance of the coated sheet. However, dark lines, or striations are often observed on the surface of the galvannealed sheet even when operating with a new, unblemished sink roll. An example is shown in Fig. 2. These dark striations mirror the machined grooves on the sink roll, and when they occur, render the finished galvanneal sheet product unsuitable for critical applications such as the exposed, painted parts of automobiles. This study examines the origin of such sink roll related striations, explains their occurrence on the basis of the reactions occurring during galvannealing, and proposes methods to reduce their occurrence.

2. Experimental procedure

Striations were observed on galvanneal during a production campaign on a commercial hot-dip line, and a representative sample was obtained from a coil for analysis. Aluminium is typically added to galvanizing baths to control the galvanizing and galvannealing kinetics [2], and the aluminium content of the zinc bath at the time the sample was processed was between 0.14–0.15 wt %. This level of aluminium is normal for galvanizing baths but slightly higher than normal for the production of galvanneal [2]. Other processing parameters such as the thickness of the coating, the temperature and time at which the galvanized sample was galvannealed, and all other production parameters were set at typical optimum values for the production of the galvannealed product. The steel substrate on which the coating was applied was a vacuum degassed, ultra-low carbon, titanium and niobium stabilized steel grade that is extensively

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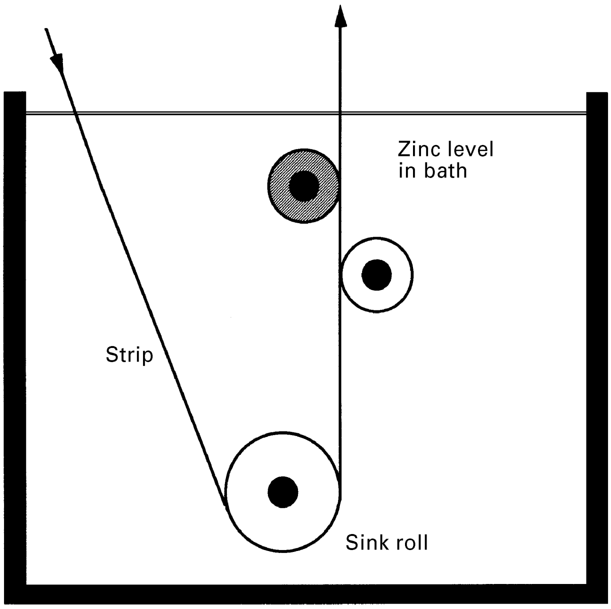

Figure 1 Schematic view of steel sheet in a continuous galvanizing bath.

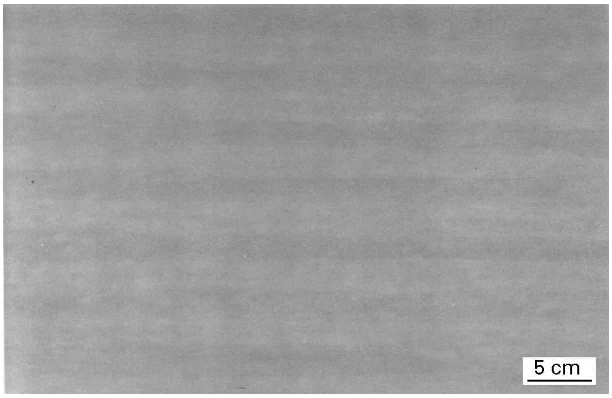

Figure 2 Macro-photograph of surface striations on the surface of galvannealed steel sheet.

used in the production of automobiles. The samples with the striations were examined in the laboratory utilizing a variety of analytical techniques.

The chemical composition of the coating (iron and aluminium contents) in the light and dark areas of the surface was determined by selectively dissolving the coating in those areas in inhibited HCl, and analysing the solution by flame atomic absorption (AA). The coating mass per unit area was also obtained from this procedure.

Optical metallography and scanning electron microscopy (SEM) were used to characterise the coating microstructure in cross-section. The details of the metallographic preparation technique are described in reference [3]. The surface of the coating was also examined in planar view using an Amray 1600 scanning electron microscope (SEM).

Auger electron spectroscopy (AES) in conjunction with sputter depth profiling for elemental analysis was carried out on the samples using a Perkin-Elmer physical electronics Model 590A scanning Auger microprobe.

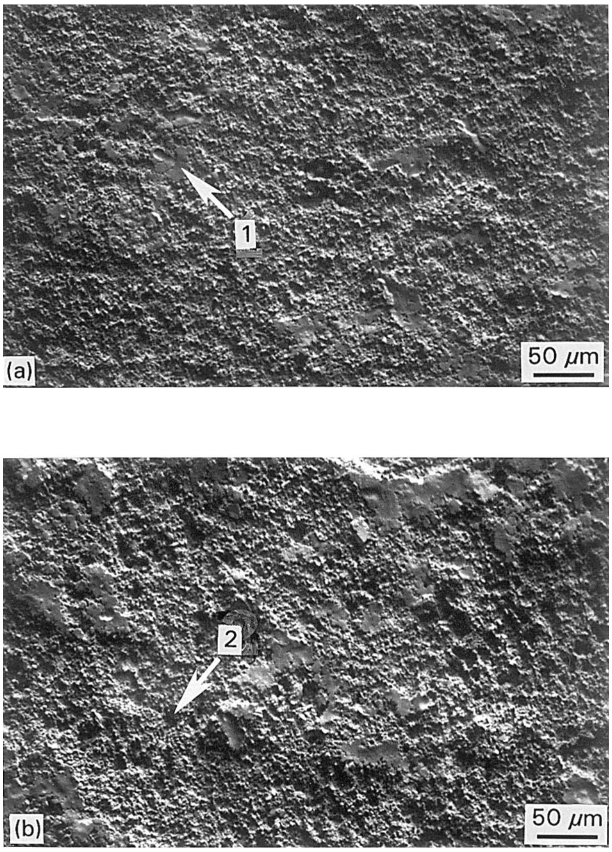

Figure 3 SEM micrograph of (a) Surface of a light area on the sheet surface, (b) surface of a dark striation on the sheet surface. Note burnish marks (1) and craters (2).

3. Results and observations

SEM micrographs of the light and dark areas that constitute the striations on the surface of the coating are shown in Fig. 3 (a and b) respectively. A combination of backscattered and secondary electron signals were used for imaging in the SEM to present a better view of the topography of the coating in the dark and light areas. The inherent roughness of the surface of galvanneal coatings is evident in both the light and dark areas. Areas of the surface also appear to be burnished, which is also a typical feature of such coatings that have been through a galvanneling line and have undergone skin-pass or temper rolling. The difference between the two surfaces as shown in Fig. 3 (a and b) visually appears to be an increased roughness in the dark area when compared with the light area. This increased roughness in the dark area is the result of numerous small craters or pits that have been identified in Fig. 3 (a and b). On observation at higher magnifications, shown in Fig. 4 (a and b), the crystals of the iron–zinc δ phase intermetallic [4] are clearly seen in both areas, with a crater, or pit in the dark area shown more clearly in Fig. 4b. It is therefore evident that the darker areas on the sheet surface appear so because of the greater roughness of the coating. The larger number of surface pits would reduce the amount of reflected light, to cause those regions to visually appear darker than the adjacent coating regions and therefore give rise to the striated appearance. Optical metallography of the cross-sections of the coatings also confirmed the rougher nature of the dark areas of the coating.

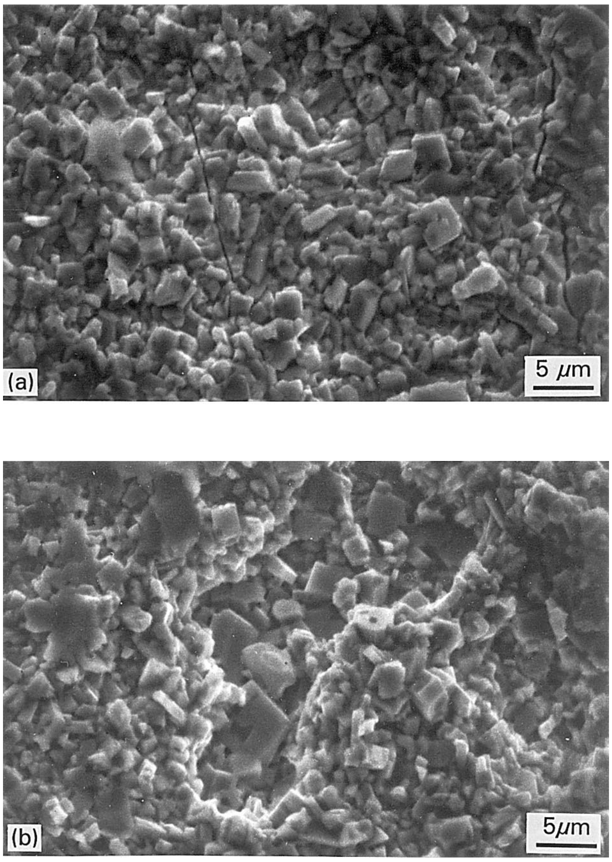

Figure 4 SEM micrograph of (a) a higher magnification view of the surfaces of (a) light area and (b) dark striation on the sheet surface.

AES elemental depth profiles for aluminium, oxygen and iron are shown in Fig. 5(a–c). These are representative profiles from analyses carried out on duplicate samples of each of the light and dark areas. The results of the analyses indicate that the dark areas have a greater concentration of aluminium and oxygen at the surface, and less iron, especially with increasing depth profiling, when compared to the light areas. The differences observed are slight, but consistent enough to be noted.

The results of the wet chemical analysis of the light and dark areas are listed in Table I. Two samples, 0.004 square meters each, of each of the light and dark areas were analysed for the listed results. The coating in the light areas is slightly thicker than in the dark areas. The aluminium content of the light areas are lower than that of the dark areas and the dark areas also contain less iron. These results are consistent with the previous observations from the AES analyses. Since the process of galvannealing involves the interdiffusion of iron and zinc, the differences in the iron and aluminium contents of the two areas implies a difference in the kinetics of the formation of the coating in the two areas.

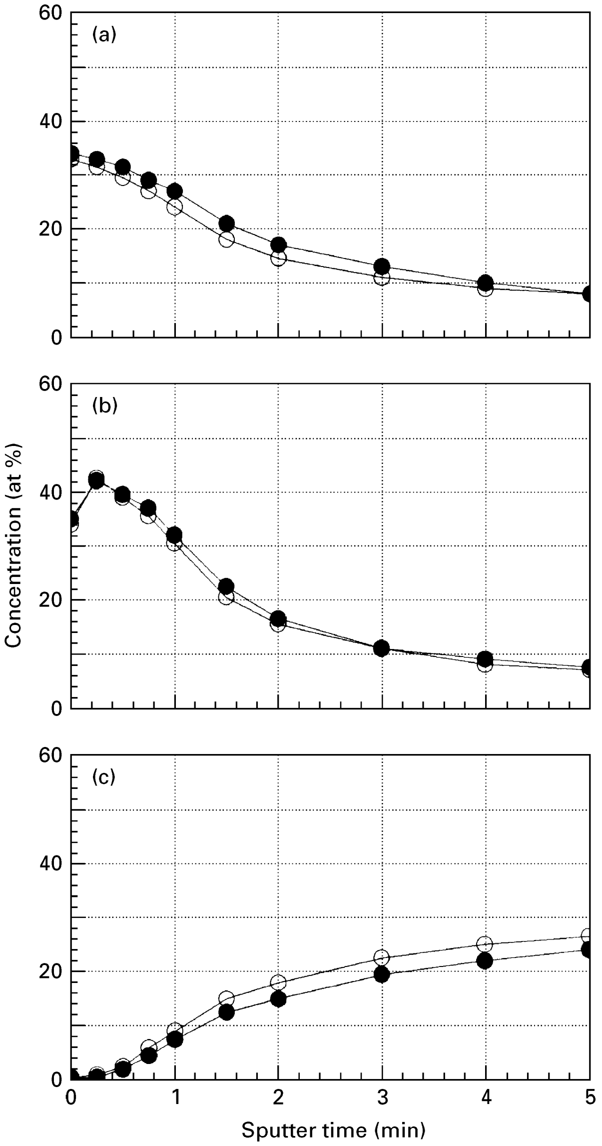

Figure 5 Elemental depth profiles of the surface of the sheet determined by AES (a) aluminium, (b) oxygen and (c) iron in all cases data taken from a dark area is denoted by the symbol (●) and data from a light area is denoted by the symbol (○).

TABLE I Chemical analysis of the light and dark areas of the coating

Sample	Coating Chemistry			
	Coating mass (g m^{-2})	Iron (g m^{-2})	Al (wt %)	Al enrichment (g m^{-2})*
Light Area 1	70.4	8.3	0.32	0.12
Dark Area 1	65.6	7.9	0.36	0.14
Light Area 2	69.4	8.5	0.32	0.12
Dark Area 2	63.3	7.7	0.36	0.14

*Al Enrichment = (Al in actual coating) − (Al based on a 0.145% Al bath)
= ((wt % Al × Coating Mass) − (0.145 × Coating Mass))/100

4. Discussion

When the steel strip first contacts the molten galvanizing bath, the first reaction observed to occur on the surface of the strip is the reaction with the small amount of aluminium in the predominantly zinc melt to form an iron–aluminium intermetallic layer [5, 6]. The formation of this iron–aluminium intermetallic layer on the sheet surface isolates the sheet from further direct contact with the zinc melt. In effect, the iron–aluminium layer is a diffusion barrier that prevents the formation of iron–zinc intermetallics by preventing the interdiffusion of the zinc in the melt and the iron in the steel sheet. Since iron–zinc intermetallics are undesirable in a galvanized product [2], the formation of the barrier layer is advantageous when the objective is to produce purely a zinc coated (galvanized) product. If the objective, as in this case, is to produce an iron–zinc coated product (galvanneal), the sheet is further annealed at temperatures between 480–535 °C [2]. This annealing, or galvannealing, causes the breakdown of the iron–aluminium diffusion barrier layer, and facilitates the formation of iron–zinc intermetallics, until the whole zinc coating has been fully transformed by diffusion into a series of intermetallic phases in accordance with the iron–zinc phase diagram [4]. The amount, and coherence of the initial diffusion barrier layer formed on the steel surface influences its breakdown and the subsequent diffusion reactions. The formation of the barrier layer is known to be influenced by various factors such as the micro-chemistry of the surface of the steel sheet, the amount of aluminium, dissolved in the zinc melt, the temperature of the steel sheet entering the bath etc. [7]. Non-uniformity in the formation and breakdown of the iron–aluminium barrier layer leads to non-uniform iron–zinc interdiffusion and results in an undesirable surface appearance on galvanneal [8].

The contact of the grooved sink roll with the steel sheet in the zinc bath selectively suppresses the formation of the iron–aluminium barrier layer on the sheet surface. Since the roll is grooved, there is no direct contact between the roll and the sheet in areas of the grooves and significant contact in the other areas. Fig. 6 shows a schematic view of this differential contact and the result that it might have on the iron–aluminium barrier layer formation. The increased pressure at the areas of contact between the roll and the strip could lead to a decreased formation of the iron–aluminium layer in those areas. Additionally, the mechanical contact and possible abrasion could either cause cracking and damage to any barrier layer already formed, or even completely destroy the layer in the areas of contact. However, in the area of the grooves, where there is no contact between the roll and strip there is free, unrestricted growth of the barrier layer. There is also increased aluminium transport within the groove areas because of greater fluid flow in the grooves during normal operation (rotation) of the roll. These facts suggest that differential growth of the iron–aluminium layer barrier layer could occur because of the contact of the sink roll with the sheet.

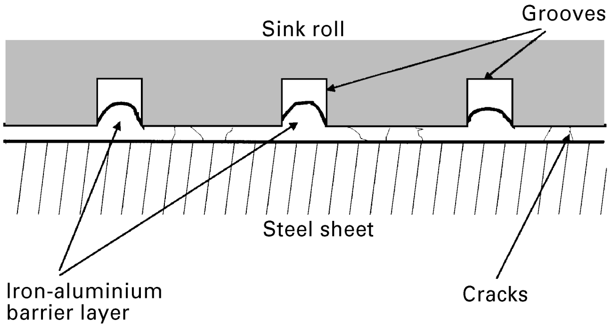

Figure 6 Schematic view (not to scale) of the contact of the sink roll with the sheet and its effect on the iron–aluminium layer growth.

The non uniform formation of the iron–aluminium intermetallic barrier layer affects the subsequent growth of the iron–zinc intermetallics by causing a lower amount of interdiffusion and alloying to occur in those areas of the sheet that have a thicker or undamaged iron–aluminium barrier layer. This is seen in the results listed in Table I which show that the dark areas, corresponding to the grooves, have a higher amount of aluminium resulting in a lower amount of iron interdiffused to the final coating when compared with the lighter areas. This effect in itself does not explain the rougher coating in the dark areas, but serves to confirm the hypothesis about the differential formation of the iron–aluminium barrier layer on the sheet surface. This indirect confirmation of the hypothesis is, to a large extent, the only way to determine the non uniformity of the sub-micron thick barrier layer which is destroyed during the galvannealing process.

The amount of the iron–aluminium barrier layer formed on the sheet surface is dependent on various factors, the most important of which is the aluminium concentration of the zinc bath [7]. It has been observed in our laboratory in other studies (Fig. 7(a and b)) that higher concentrations of aluminium in galvanizing baths, around 0.15 wt % and higher, cause the iron–zinc intermetallics to form non-uniformly, resulting in an uneven coating surface after galvannealing. This is a result of aluminium destabilizing the planar interface between the liquid zinc and the iron–zinc intermetallics growing by diffusion. The

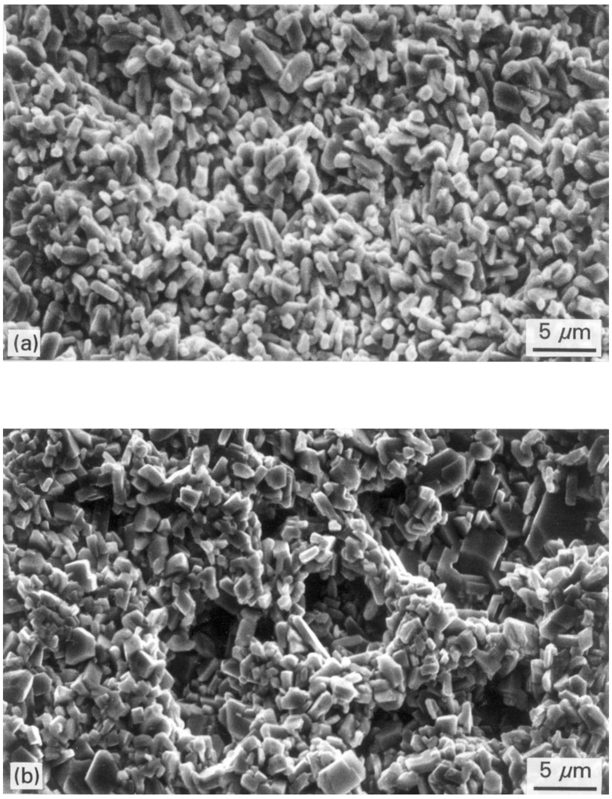

Figure 7 Surface of laboratory produced galvanneal sheet from (a) a low aluminium containing zinc bath and (b) a high aluminium containing zinc bath.

result of the non-planar interface is a pitted appearance of the coating surface after the iron-zinc intermetallics have consumed all of the pure zinc layer by diffusive growth. Lower aluminium levels in the galvanizing bath do not appear to destabilize the interface to the same extent, and the resultant coating surfaces lack the pitted appearance characteristic of galvanneal coatings produced from higher aluminium baths. Fig. 7(a and b) show the surfaces of laboratory produced galvanneal coatings, produced from a very low aluminium containing zinc bath (0.03 wt % Al) and a higher aluminium content zinc bath (0.14 wt %). The other processing conditions were held constant.

Thus, the striations on the surface of the commercial galvanneal samples can be explained on the basis of the differential formation of the iron–aluminium barrier layer at the steel-bath interface during galvanizing. The contact of the sink roll with the steel sheet causes variations in the iron–aluminium barrier layer at the interface, with a more coherent layer formed in the areas where there is no contact i.e., the areas of the grooves on the sink roll. As a result, when the sheet is galvannealed to form iron–zinc intermetallics, the coating in the groove regions develops under a local environment of higher aluminium concentration than the adjacent areas. This growth of the iron–zinc coating under a higher local aluminium concentration leads to a greater pitted surface appearance in those areas, as shown in Figs 3b and 4b, and results in the formation of dark striations on the surface of the coated sheet.

To mitigate the striations on the surface, variations in the formation of the iron–aluminium barrier layer must be minimized. The contact of the steel sheet with the sink roll is essential to the processing, but the pressure exerted by the roll on the sheet can be minimized during the processing to reduce the amount of damage to the barrier layer at the areas of contact. Lowering the aluminium content of the zinc bath would minimize the growth rate of the iron–aluminium barrier layer and would therefore reduce the non-uniformity in its formation. The aluminium content of the bath should therefore be maintained at the lowest level possible. This would enable a reduction in the variation of the iron–aluminium barrier layer on the sheet surface. Since lower aluminium levels in general give rise to a coating surface lower in pits, even a local increase in aluminium level at the areas of the roll grooves will not result in rougher coating in those areas, and therefore will not give rise to dark striations.

5. Conclusions

The formation of dark striations on the surface of galvanneal coated steel sheet as a result of contact with a sink roll is because of the formation of a non-uniform iron–aluminium intermetallic layer on the steel surface during the galvanizing process. The non uniformity in this iron–aluminium diffusion barrier layer mirrors machined grooves on the sink roll, with a greater amount of the barrier layer being formed in the areas of the sheet corresponding to the grooves on the sink roll. The greater amount of the barrier layer results in non-uniform diffusional growth of iron–zinc intermetallics during subsequent galvannealing, which results in a rougher coating surface. The rougher coating surface appears darker in reflected light, giving rise to the striated appearance of the coated sheet after processing. The striations can be minimized or eliminated by adjusting processing parameters to minimize the overall growth rate of the iron–aluminium barrier layer during galvanizing to minimize the differential growth observed because of sink roll contact. Lowering the overall aluminium content of the galvanizing bath would lower the growth rate of the barrier layer. It would also ensure that in the areas where a greater amount of the barrier layer forms, the amount of the barrier layer is still insufficient to cause significant coating roughness after the growth of the iron–zinc intermetallics during subsequent galvannealing. The result would be a desirable lack of striations on the finished galvannealed steel sheet product.

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