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Investigation of Streaky Mark Defect on Hot Dip Galvannealed IF Steel

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Interstitial-free (IF) steels are widely used for car body material. However, a few types of streaky mark defect are commonly found on hot dip galvannealed (GA) IF steel sheets. In the present study, both the phase structure of a streaky mark defect and the microstructure of the substrate just below it were characterized by optical microscopy (OM) and scanning electron microscopy (SEM). It was found that the bright streaky mark area was composed of δ phase while the dark normal area was full of craters. More than half of the grains at the uppermost surface of the substrate just below the streaky mark defect are unrecrystallized grains which could result from lower finish rolling temperature during hot rolling and be kept stable during the annealing process, while almost all the grains in the normal area are equiaxed grains. In order to confirm the effect of the unrecrystallized grains on the coating morphology, hot dip galvannealing simulation experiments were carried out in IWATANI HDPS. It is proved that the unrecrystallized grains accelerate the Fe-Zn reaction rate during galvannealing and result in a flatter coating surface and an even coating thickness. Finally, a formation mechanism of the streaky mark defect on the hot dip galvannealed IF steel sheet was discussed.

Keywords *: IF steel, galvannealed(GA), coating, galvanized(GI)*

1. Introduction

Hot dip galvannealed (GA) interstitial-free (IF) steel is widely used for outer panels in automobile industry due to its excellent formability, weldability and paintablity. The GA coatings are essentially diffusion coatings that expose the hot dip galvanized (GI) steel to an annealing temperature around 500℃ to produce a fully alloyed coating containing Fe-Zn intermetallic phases.[1] As a matter of fact, due to the additional Fe-Zn reaction after hot dip galvanizing, more variables should be considered to obtain a good surface appearance and a high resistance of powdering. Besides the processing variables and zinc bath chemistry, the surface quality of the substrate just before dipping has strong effect on the coating quality.[2]

Among all the regular coating defects, the so called 'streaky mark' is a very famous one which behaves as dark and white streaks parallel to the rolling direction (RD) and could not be covered after painting. So in the past two decades, the different causes and control measures of streaky mark defect have been well studied. T Nakamori[3] suggested that the streaky mark results from an influence of fine crystal grains in the surface layer of the Ti-IF steel.[4] However, K Tahara[5] found that the mean size of the crystal grains in the surface of the steel sheet just below the portion having the streaky mark is larger than that in the normal portion. He suggested to control both the size distribution and texture distribution of ferrite grains in the uppermost layer of the substrate steel, that is, the more even these two distributions are, the less inconspicuous the streaky mark becomes. In recent studies, M. H. Hong[6),7] found that the occurrence of streaky mark is strongly related to the Mn and Si oxides at the interface of coating/substrate and the ultrafine grains at the extreme surface of the steel substrate, especially for the high strength IF steels. It is generally accepted that the chemical composition of the steel substrate has great effect on the Fe-Zn reaction, for example, if the content of Ti is too high, the streaky mark becomes worse; however, when it is partially replaced by Nb, it can be effectively prevented.[5] Moreover, B addition can inhibit the outburst reactions at the grain boundaries and thus the streaky mark defect being prevented as well. However, it is still a challenge to eliminate this type of defect in the production

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practice.

In present study, a streaky mark defect formed on hot dip galvannealed Ti-added IF steel was investigated, and the cause of the defect was proved by hot dip galvannealing simulation experiments. And a formation mechanism of the streaky mark was discussed based on the results.

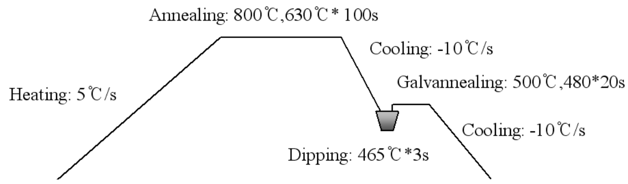


Fig. 2. Thermal cycles of the hot dip galvannealing experiments.

2. Materials and experimental procedures

A GA coating sample with obvious streaky mark as shown in Fig. 1 was obtained from continuous galvanizing line (CGL). The streaky mark defect area which is about 30 mm wide looks a little brighter than the normal area. The chemical composition of the base steel is shown in Table 1 and the coating weight was 45 g/m^2 per side. The surface and cross-sectional morphologies of the coating and the interface morphology after GA coating removed by 25%HCl solution with an addition of the inhibitor ($(CH_2)_6N_4$) were investigated using a Leica optical microscope (OM) and Hitachi S4200 scanning electron microscopy (SEM). To investigate the ferrite grains at the uppermost surface of the substrate, both samples which are slightly polished and longitudinal section samples were prepared. The grains were revealed by saturated picric acid solution and were observed by OM.

To confirm the effect of the substrate grain structures on the streaky mark defect, hot dip galvanizing and galvannealing experiments were performed in an IWATANI Hot Dip Process Simulator (HDPS). The substrates for galvanizing were cut from the full hard IF steel sheet with the same chemical composition as shown in Table 1 and had a length of 220 mm and a width of 120 mm. Prior to the galvanizing procedure, the samples were fully degreased and rinsed. The thermal cycles are shown in Fig. 2. First of all, two different annealing temperatures (800 ℃ and 630 ℃) were used to create two different grain structures of the base steel just before hot dipping. The annealing atmosphere was a mixture of 10%H_2 and 90%N_2 with the dew point of -30 ℃. Secondly, two different galvannealing temperatures (500 ℃ and 480 ℃) were used to get different alloy extents of the coating. Surface morphology and cross sectional morphology of the coating were observed by OM and SEM and were compared with those of the defect samples.

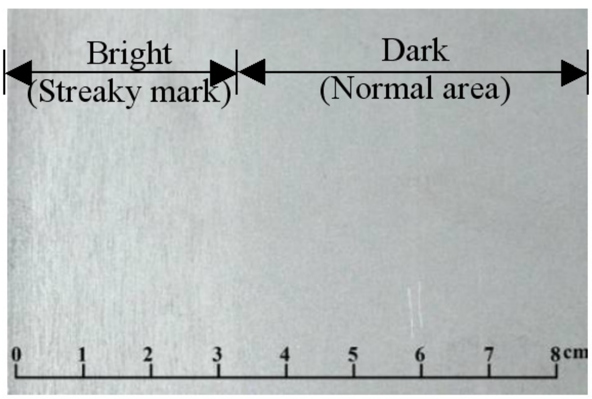


Fig. 1. Bright streaky mark obeserved on GA coating.

Table 1. Chemical composition of the base steel sheet (wt%)

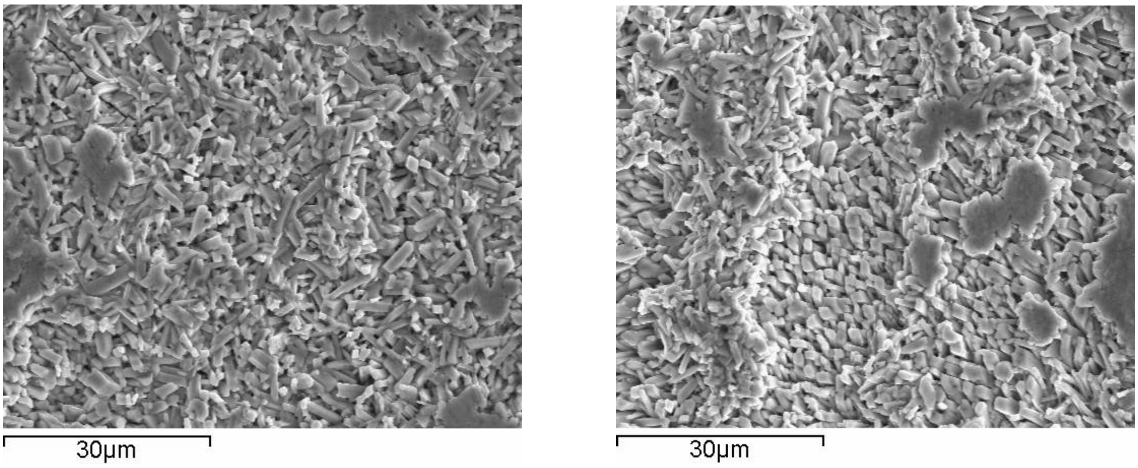
C	Si	Mn	P	S	Ti	B
≤0.002	≤0.03	0.1~0.2	≤0.012	≤0.01	0.05~0.07	0.0003

3. Results and discussion

3.1 Features of the streaky mark defect

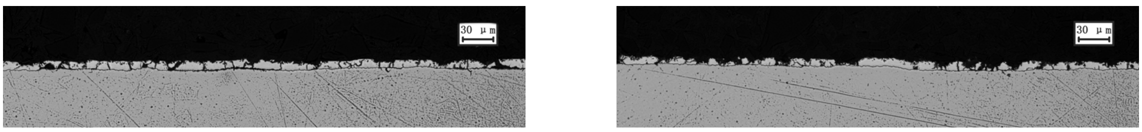
Both the surface morphology and the cross sectional morphology of the GA coating observed on the streaky mark and normal area are shown in Fig. 3 and Fig. 4. In the streaky mark area (Fig. 3a), the Fe-Zn phase is random delta phase. However, in the normal area (Fig. 3b), both random delta phase and ordered zeta phase are included, as a result of which, a typical crater morphology was formed. At the base of the craters locate some ordered zeta phases and the coating thickness of the craters is much smaller than the surrounding coating which is composed of random delta phases. As a result, the coating surface of the streaky mark area is much flatter and the coating thickness is much more even than those of the normal area, as shown in Fig. 4a and Fig. 4b. These two different coating morphologies have totally different effect on the reflection of light and cause the color difference between the streaky mark and normal area.

The interfaces of the coating/substrate after zinc coating being removed by HCl with addition of inhibitor are shown in Fig. 5. Being similar to the surface morphology difference between the streaky mark and normal area, the interface of the streaky mark area is much more even than that of the normal area. As a matter of fact, the even interface of coating/substrate predicates a uniform Fe-Zn phase growth rate during the galvannealing progress. However,



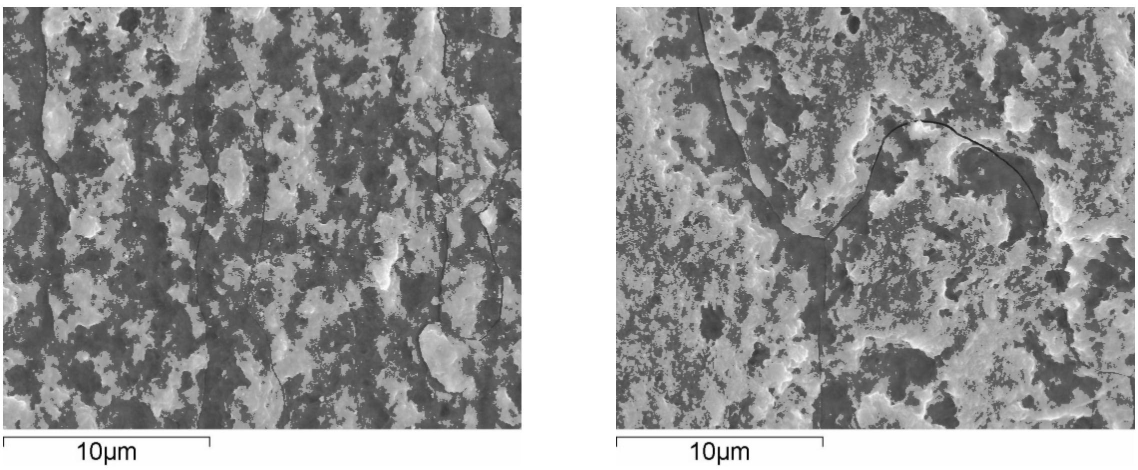
(a) (b)

Fig. 3. Surface morphologies of the GA coating (a) streaky mark and (b) normal area.



(a) (b)

Fig. 4. Cross sectional morphologies of the GA coating (a) streaky mark and (b) normal area.

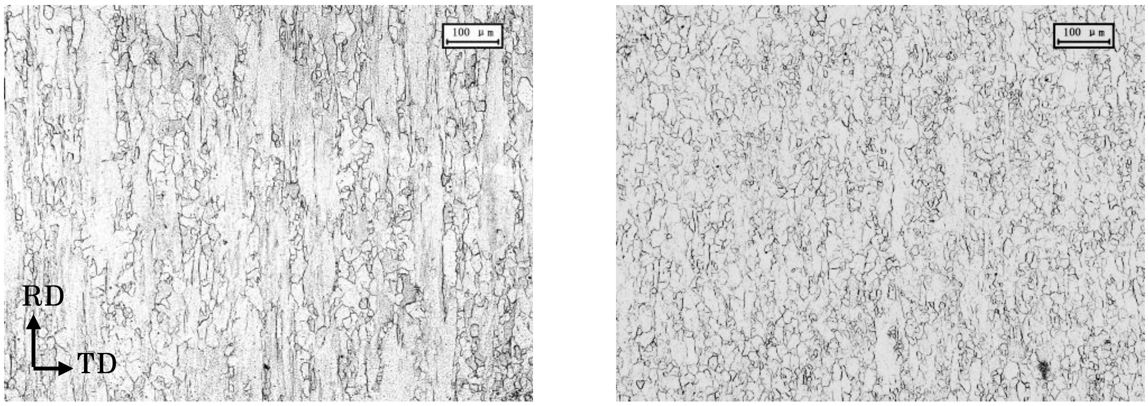


(a) (b)

Fig. 5. Interface morphologies of the substrate after GA coating being removed (a) streaky mark and (b) normal area.

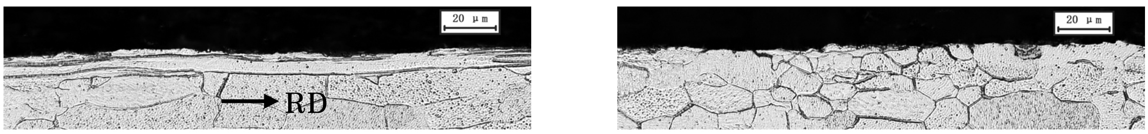
in the normal area, the Fe-Zn phase growth rate at the grain boundaries is much faster than that at the grain interiors. As a result, it is easy for the outburst structures to form at the grain boundaries. And plateaus which are corresponding to the bases of the craters in the coating form at the grain interiors.

The substrate grains of the uppermost surface are shown in Fig. 6 and Fig. 7. About half of the grains in the streaky mark area are elongated grains, while almost all the grains in the normal area are equiaxed grains. Because the sample was slightly polished during the procedure of sample preparation, the real percentage of the elongated grains may be even higher than half. From the longitudinal section view, almost all the uppermost surface in the streaky mark area was covered with a layer of elongated grains whose total thickness is less than 10 μm. Based on Fig. 6a and



(a) (b)

Fig. 6. Substrate grains of the uppermost surface (a) streaky mark and (b) normal area.



(a) (b)

Fig. 7. Longitudinal section substrate grains (a) streaky mark and (b) normal area.

Fig. 7a, the dimensional size of the elongated grains could be measured. As shown in Fig. 8, the average length-width ratio of the elongated grains is about 4.9, which is very close to 5, the calculated length-width ratio of the grains after cold rolled with a reduction rate of 80%. It can be concluded from the shape and size of these elongated grains that they could be some unrecrystallized grains remained from the recrystallization annealing before hot dip galvanizing. Because of the existence of these unrecrystallized grains at the uppermost surface, the Fe-Zn reaction kinetics in the area could be totally different from that in the normal area. According to the coating morphologies and interface morphologies observed in this study, it seems that these unrecrystallized grains can reduce the difference between the grain boundary and grain interior, as a result of which, the growth of the Fe-Zn phase become more even and the crater density is effectively reduced.

The source of the unrecrystallized grains at the uppermost surface could be traced back to the hot rolling. Generally, the temperature of the surface layer is a little lower than that of the inner side of the hot strip, especially at the strip edges. When finish rolling temperature is not high enough, it is possible for the surface layer to drop into the mix region of austenite and ferrite. Those grains which are hot rolled below Ar3 temperature could result in the formation of stable end orientation of ferrite which is hardly to recrystallize during annealing.

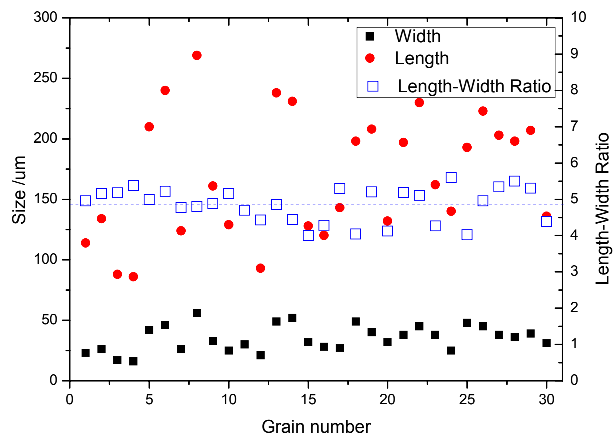
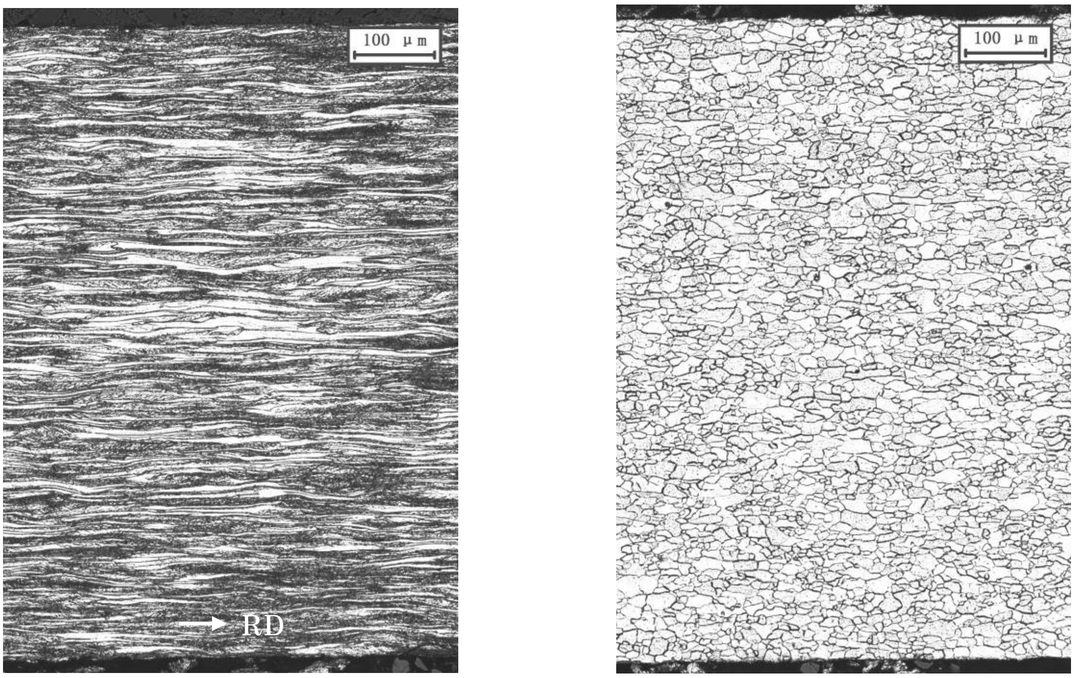


Fig. 8. Dimensional size of the elongated grains at the uppermost surface.

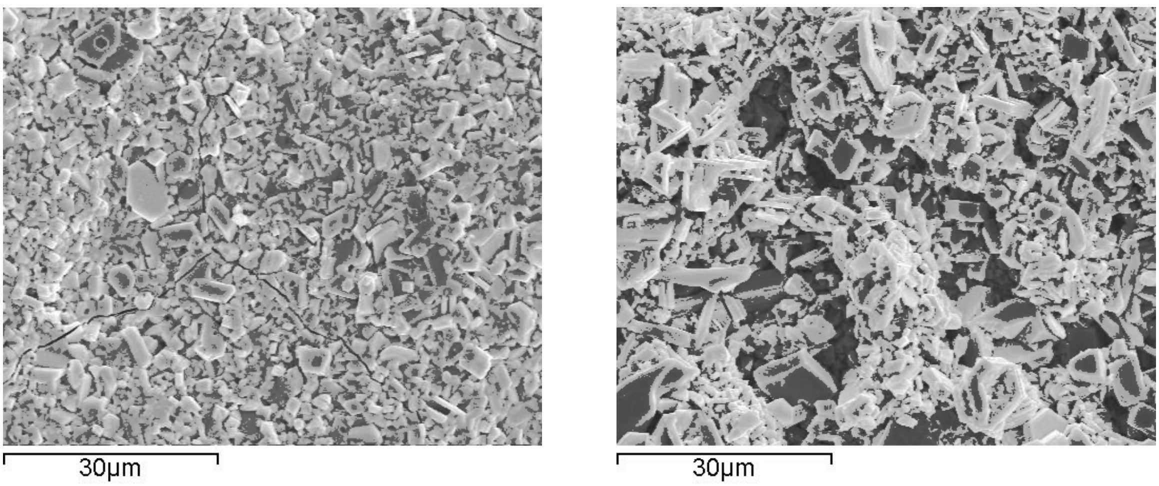
3.2 Effect of the unrecrystallized grains on the coating morphology

To investigate the effect of the unrecrystallized grains at the uppermost surface of the steel on the coating morphology, samples were annealed at different temperatures to obtain different grain structures. When the full hard cold rolled steel sheet was held at 630 ℃ for 100s, it was not high enough for the grains to complete recrystallization and totally unrecrystallized grains remained, as shown in Fig. 9a. However, when held at 800 ℃, all the grains have



(a) (b)

Fig. 9. Grain structures of the substrates annealed at different temperatures a) 630 ℃ b) 800 ℃.



(a) (b)

Fig. 10. Surface morphologies of the GA coating formed on a) unrecrystallized grains and b) equiaxed grains.

turned into equiaxed grains, as shown in Fig. 9b. Though the origin of the unrecrystallized grains in the experiment is different from that of the unrecrystallized grains at the uppermost surface just below the streaky mark defect area, their effects on the coating morphology should be similar.

After these two samples went through the same hot dip galvanizing and galvannealing procedure, the GA coatings were achieved. The surface and the cross sectional morphologies of the GA coatings were shown in Fig. 10 and Fig. 11 respectively. Because the substrate used in the experiment is Ti-IF steel, the coating morphology with a great amount of craters takes place frequently. As a result, the thickness of the coating formed on the equiaxed grains is not so even. However, the surface of the coating formed on the unrecrystallized grains is smooth and the thickness of which is even. The coating difference between the two samples is almost the same as that between the streaky mark and normal area on the defected steel sheet examined

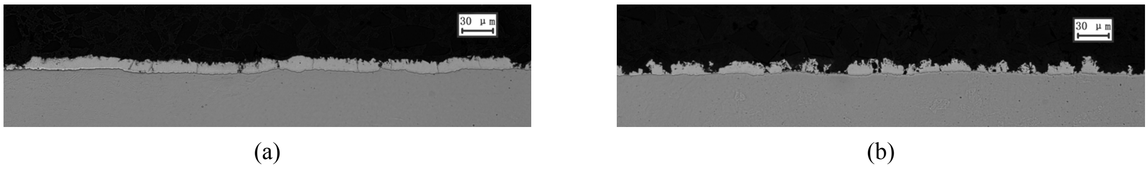


Fig. 11. Cross sectional morphologies of the GA coating formed on a) unrecrystallized grains and b) equiaxed grains.

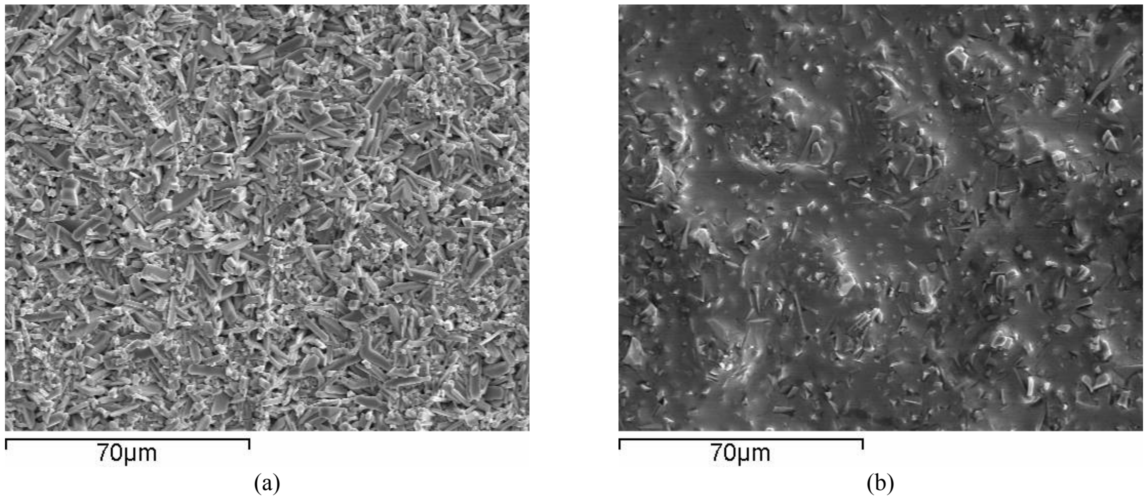


Fig. 12. Surface morphologies of the GA coating galvannealed at 480 ℃, formed on a) unrecrystallized grains and b) equiaxed grains.

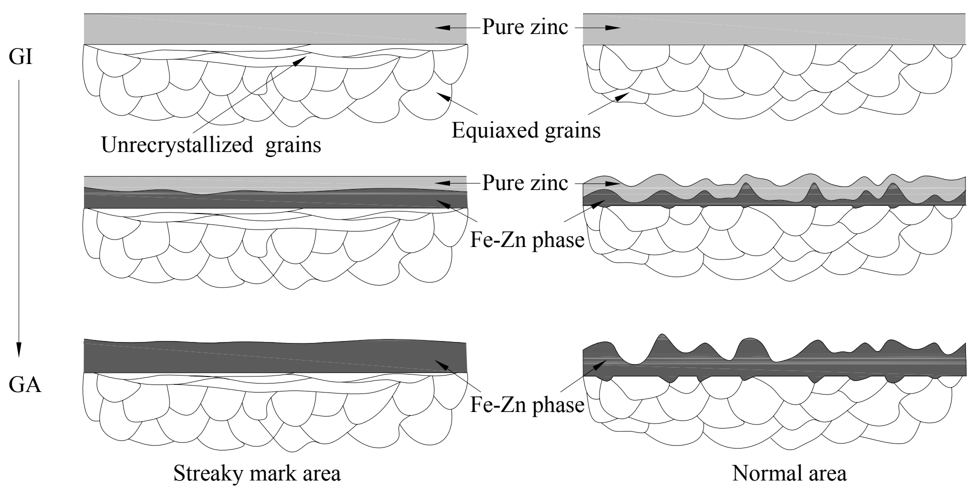


Fig. 13. Schematic of the formation mechanism of the streaky mark defect.

above. However, due to the galvannealing parameters used in the experiments could not be absolutely the same as those used in the production line, the phase structure of the coating achieved by experiment is a little different from that of the sample from the production line. It seems that the alloying extent of the coating in the experiment is a little higher. Nevertheless, it is proved that the unrecrystallized grains and the equiaxed grains have different effects on the GA coating morphology.

By decreasing the galvannealing temperature, the alloy extent of the coating also decreased. As shown in Fig. 12, when galvannealed at 480 ℃ for 20s, all the eta phase in the coating formed on the unrecrystallized grains has turned into Fe-Zn phase, however, there still remained a layer of eta phase in the coating formed on the equiaxed grains. It is clear that the unrecrystallized grains accelerate the growth rate of Fe-Zn phase during galvannealing.

The formation mechanism of the streaky mark defect investigated in this paper is shown in Fig. 13. When there is a thin layer of unrecrystallized grains at the uppermost surface, the microstructure of the surface which has great effect on the morphology of the hot dip galvannealed coating is completely different from that of the normal area where all the grains are equiaxed grains. In the normal case of the equiaxed grains, especially for Ti IF steel, the grain boundaries are the fast diffusion paths of the Fe-Zn reaction, resulting in outburst structures at the grain boundaries. With the additional effect of the texture on the coating morphology, craters frequently form in the coating. However, in the abnormal case of the unrecrystallized grains at the uppermost surface, it seems that the difference between the grain boundaries and the grain interiors is not so obvious, as a result of which, the growth rate of the Fe-Zn phase at the grain boundaries is close to that at the grain interiors. Moreover, the unrecrystallized grains accelerate the average growth rate of the Fe-Zn phase. A coating with a flatter surface and a more even thickness in microscopic scales forms on the unrecrystallized grains. The different coating morphologies have different effects on the reflection of light and cause the color difference between the streaky mark and normal area in the end.

4. Conclusions

A certain type of streaky mark defect observed on the GA coating surface of IF steel was characterized by OM and SEM. And hot dip galvannealing simulation experiments were carried out to confirm the cause of the defect. The following conclusions can be drawn from the results of this work.

(1) The coating surface of the streaky mark area is much flatter and the coating thickness is much more even than those of the normal area. It is the difference of the coating surface that leads to color difference between these two areas.

(2) More than half of the grains at the uppermost surface of the substrate just below the streaky mark defect are unrecrystallized grains, while almost all the grains in the normal area are equiaxed grains.

(3) The hot dip galvannealing simulation experiments prove the effect of the unrecrystallized and equiaxed grains on the coating morphology. Compared with the equiaxed grains, the unrecrystallized grains accelerate the Fe-Zn reaction rate during galvannealing and result in a flatter coating surface and an even coating thickness.

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