Mitigation of uncommon peel-off defects in galvanized steel sheets

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Abstract. Galvanizing defects occurring in hot- and cold-rolling procedures were studied by scanning electron microscopy and focused ion beam, and analyzed via the JMP software. The results show that, among the 200 bright spots dispersed along the hot dipping steel plate, the defect may be misidentified as zinc slag by the representation of coating surface, but there exists a tiny peel off on the matrix without oxide particles under each spot. Upon partial removal of zinc coating, a tiny iron film outcropped from the coating was revealed. As some of iron films are not adhered to the matrix, such outcrops are not detected. The cross-sectional morphology shows the formation of inhibition layer, with no oxide between the peel off and matrix. The relative cold and hot rolling plates are also analyzed to trace the source, that the defect is inherited from hot rolling process according to the results. By using JMP to calculate the relationship of hot rolling parameters with the defect, slab heating temperature is concluded as a strong correlation condition. The high slab heating temperature ensures smooth rolling procedure, but the intergranular binding force is too low, which enhances the coating surface separation from the matrix. After reducing the slab heating temperature from 1350 to 1300°C or lower, and optimization of descale and pickling parameters, the occurrence ratio of bright spot defects caused by peel-off was significantly reduced.

1. Introduction
The requirements for surface coatings get stricter each year [1]. For hot dip galvanizing steel strip, the surface quality, mechanical properties, size precision, shape and adherence are all very important. The surface quality of O5 on at least one side is essential for most automobiles and household appliance customers [2]. There is a number of process variables that can affect the appearance, morphology and texture of spangles. It has been reported that the nature and amount of zinc bath additions, surface topography of the steel substrate and cooling rate of the coating during solidification are the main factors, which control the final microstructure of the coating [3-6].

Recently, the researchers encountered an uncommon hot dipping defect, representing as concentrated bright spots dispersing on the whole steel plate after drawing. By analyzing the characteristics of coating surface and cross-section, those bright spots displayed different characters with common spot defects discussed in the literature [7, 8]. To achieve the generating causes of the defect, samples cutting from each procedure before galvanizing were analyzed by multiple methods in the paper. After taking several steps in response to the suspected causes, the occurrence ratio of uncommon spot defects was significantly reduced.
2. Experimental materials and procedures
Uncommon bright spot defects appear mainly in DX54D+Z or DX56D+Z galvanized steel sheets, which are used for production of automotive outer plates. Without drawing and sanding, these defects remain undetected. The characteristics of the defects were analyzed first, from coating surface, partial and total removal of zinc, coating cross-section, cold rolling surface, pickling surface, hot rolling surface, and matrix cross-section. Then, the suspected process parameters were statistically analyzed by JMP software.

Firstly, we analyzed the hot-dip galvanizing steel surface. The defect regions appeared as bright spots were carefully cut from the sheet and pre-cleaned by ultrasonic cleaning with ethanol. A visual observation was carried out on the defect areas of the coating. The macroscopic images displayed that, the bright spots dispersed along the whole plate without orientation, and the macro sizes were about 1-2 mm for different coating thicknesses. The defects are whitish grey in color, easily visible for naked eyes. Few samples (20×20 mm) were cut out using a diamond wafer blade from the defect region, analyzing the surface of Zn coating, semi-dissolved Zn and fully dissolved Zn by scanning electron microscopy (SEM). The cross-sectional samples were cut by the focused ion beam (FIB) to analyze the morphology and elemental distribution under the coating.

Secondly, the analysis of cold rolling steel surface was conducted. The suspected coil of cold rolling sheets before galvanizing was cut to small pieces, in which some samples were annealed in laboratory for comparison with the cold-rolled samples and to observe the evolution of the defect. The simulated annealing parameters were as follows: heating to 800°C and holding for 60s, cooling to 480°C with 20°C/s cooling rate and holding for 30s, then cooling to room temperature. Few cold-rolled surface (CRS) and simulated annealed surface (SAS) samples (20×20 mm) were treated by ultrasonic cleaning with ethanol, using SEM with magnification larger than 500 × to find out in the whole surface if there were the same defects with coating samples.

Thirdly, the analysis of hot-rolled surface was performed. The suspected coil of hot rolling sheets was cut to 40×40 mm pieces. The samples were immersed into hydrochloric acid with 20% density for 5 min to wash through the iron scale. The hot rolled surface (HRS) and cross-section (HRC) morphology were analyzed by SEM.

Finally, the analysis of suspected process parameters was performed. To understand the relativity of pickling and hot rolling process parameters with the generating causes of the defect, multiply data were collected and calculated by JMP, an Interactive Visual Statistical Discovery Software Series produced by SAS (Statistical Analysis System Institute, Inc.).

3. Results

3.1. Characteristic of coating surface

![Figure 1](image-url). Surface morphology and element distribution of coating: (a) coating macroscopic, (b) zinc hemi-dissolved, (c) zinc wholly dissolved.
The macroscopic morphology of the studied defect reflected as bright spot after drawing and sanding. The sizes of these spots were no larger than 2 mm. Although the spots dispersed all over the plate surface, the spots were flat and not visible under secondary electron image (figure 1(a)). The chemical compositions were sophisticated, including Al/Fe/Zn, Fe, Fe/Zn, O/Al/Zn, which were easily be considered as floating or surface zinc slag.

However, the inner surface had an interesting representation. When the zinc coating was hemi-dissolved, there was an iron film outcropped (figure 1(b)). The element distribution displayed that, the main element of the outcropped film was Fe, with little Al. By observing more than 20 samples with 10 spots each, there appeared majority of iron films representing as outcropping or floating. By accurately locating the outcropped films, there existed a tiny peel off on the matrix in the exact position of each outcropped film (figure 1(c)). The tiny peel off can be observed when the iron film was outcropped and was no observed when it was floated.

3.2. Characteristic of coating cross section
According to the coating surface analysis, the size of the tiny peel off was 20 to 100 μm with no orientation, which is an abnormal surface for cold rolling steel. The information under the surface was studied and displayed in figure 2. Several accurately located spots caused by tiny peel off were cut layer by layer to find the interface of peel off with zinc and matrix. The peel off displayed in figure 2(a) was connected with the matrix, which was pure iron, fine grain size, and 2 μm thickness, with Fe-Al (inhibition layer) and Fe-Zn phases under it, as shown in figure 2(b). There existed no oxygen between peel off and matrix but just loose zinc, which can primarily exclude the suspected effect of melt process.

The element map distribution of Fe is presented in figure 2(c), displaying the damage of steel surface. Al continuously distributed in the interface of peel off, zinc and matrix, representing good condition of the sheet passing zinc pot. Although the peel off was connected with the matrix, by the reaction of Fe with Al (figure 2(b)), it was possible to be divorced. That is the reason why the tiny peel off can’t be observed all the time. Thereafter, the appearance of tiny peel off should be further analyzed to understand the causes.

3.3. Characteristic of cold rolling surface
As the tiny peel off was observed on the matrix, the front processes including cold rolling and hot rolling were analyzed. As shown in figure 3, the evolution of the tiny peel off from annealing, cold rolling to hot rolling was interesting. The tiny peel off after cold rolling was obvious to be observed with sharp angle and margin (figure 3(a)). After annealing, the joint between peel off and matrix became loose by stress releasing (figure 3(b)). Therefore, it is easily to understand that the tiny peel off existed before cold rolling, experienced minute alternation from cold rolling to hot dipping processes.
3.4. **Characteristic of hot rolling surface**

The suspected hot rolling samples were thereafter analyzed for more than 8 coils, as shown in figure 3(c). The tiny peel off with high density was inherited from hot rolling to the following process. The peel off was relatively larger comparing with cold rolling products. By analyzing more than 10 samples for each hot rolling coil, there was no difference of the surface morphology for the upper and down as well as the head and middle of the plate. With a large joint area between single peel off and matrix (figure 3(c)), the peel off displayed densely and tightly, resulting in difficult to be removed by scale breaking in pickling process. Therefore, the dense and compact peel off generated in hot rolling process would be reserved and magnified to cold rolling and hot dipping, making the occurrence of a compact uncommon bright spot defect.

At the same time, no other oxides, except iron oxide, were observed around the peel off, which further excluded the effect of melting process on the defect.

4. **Discussion**

4.1. **Morphology characteristics**

According to the above analysis, large amount of bright spots dispersed randomly along the galvanized steel plate after drawing and sanding. As sophisticated composition including Al, Fe, Zn, O were observed on the coating surface, it is easily to be misidentified as floating or surface zinc slag causing the formation of the defect.

However, after removing zinc coating layer-by-layer, the following results were obtained. A peel off similar to the hot rolling defect appeared, with a sharp edge and outcropped from the matrix. According the literature [9], the peel off formed on hot rolling steel plate has relatively larger size: 15~50 mm, and most of the time formed on the edge of plate [10]. The hot rolling peel off can be caused by iron scale or other metal oxides. However, those oxides were not observed in the galvanizing steel plate mentioned in the paper. Thereafter, the unknown cause of the defect needs further analysis.

4.2. **Process investigation and solutions**

According to the above analysis, the suspected causes of peel off defect resulting in bright spots dispersed explosively on the whole surface of galvanized outer plate concentrated to hot rolling procedure. The researchers collected several related information for calculation to make sure their relations with the defect, including chemical composition, slab heating temperature × time, rough rolling entry and exit temperature, and fine rolling draught pressure.

The relationship of hot rolling procedure parameters with the peel off defect was calculated by JMP, which is a powerful statistical software. By comparing the correlation of parameters mentioned above with the defect, the results showed that slab heating temperature × time is a strong correlation condition, as displayed in table 1.
Single p value was used to screen major effect when it is less than or approach to 0.05. Apparently, slab heating parameters need to be optimized according to the calculations. Otherwise, single p values of other parameters were all more than 0.05, such as final rolling, coiling temperature and et al., representing no strong correlation.

Table 1. Correlation of slab heating parameters with defect.

| Program            | Single p value | Correlation |
|--------------------|----------------|-------------|
| Slab entry temperature | 0.0121         | Yes         |
| Heating temperature        | 0.0903         | Yes         |
| Heating time           | 0.0167         | Yes         |
| Slab exist temperature     | 0.0025         | Yes         |

4.3. Mechanism of optimizing the slab heating temperature

The researchers went through the slab parameters of suspected hot rolling coils, finding that the slab heating temperatures were higher than normal coils maximized to 1320°C or even higher to 1350°C.

According to the generation mechanism of iron scale, if the surface temperature of slab is higher than 1300°C, the scale melts on the slab surface, resulting in the decreasing diffusion resistance and rising oxidation [10]. Therefore, there is a strong cohesion between the scale and matrix. As the scale is hardly removed, causing poor surface quality of the hot rolling plate. The defected surface area will be enlarged by cold rolling and hot dip galvanizing procedure, producing compact bright spot defects.

After decreasing the heating temperature by 30 to 40°C and optimizing phosphorous content between rough and fine rolling processes, the occurrence ratio of uncommon bright spot defects caused by hot rolling peel-off was significantly reduced.

Although peel-off defects still existed in the following manufacturing procedure, bright spots were no more distributed along the total plate but only a few of them were observed. The optimization provided an effective surface quality improvement, according to the above analysis.

5. Conclusions

Steel plates subjected to various procedures (from hot dip galvanizing to hot rolling) were examined, and uncommon bright spots caused by peel-off defects were detected. Their source was the abnormal slab heating parameter, and their behavior can be reduced to the following findings.

- In galvanized products, defects with a size no larger than 2 mm were dispersed all over the plate. They could be detected only after drawing and sanding. Their chemical compositions included Al/Fe/Zn, Fe, Fe/Zn, O/Al/Zn, due to which they could be mistreated as floating or surface zinc slags. After zinc coating was partially and completely, there existed tiny peel-off sites with composition of a pure iron.
- The cold rolling peel-off defects after had sharp angles and edges, and their separation from matrix occurred by stress relief after annealing.
- The hot rolling peel-off defects were dense and compact, with no other oxides, except iron oxide. The peel-off resulted in poor surface quality and the formation of compact bright spot defects during galvanizing.
- By investigating the relationship of several hot rolling process parameters and optimizing them, the occurrence ratio of defects caused by abnormal slab heating process was significantly reduced.

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