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Influence of Mechanical Surface Treatments on Sandelin Phenomenon in Silicon Containing Steels

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ABSTRACT

In this study, the influence of mechanical surface treatments on the Sandelin Phenomenon in silicon containing steels was investigated. For this purpose, various surface topographies with/without deformed zones were produced on the steel samples with different silicon contents by applying mechanical surface treatments such as grinding, and polishing in addition to conventional pickling. Hot-dip galvanized coatings formed on the conditioned surfaces were examined through cross-sections with optical microscope and scanning electron microscope. The results indicate that surface topography is the main factor controlling the stability of a hot-dip galvanizing coating and a surface topography with intermediate roughness and sharp asperities formed with abrasive particles in the range of 100 - 270 µm can produce suitable coatings on the silicon containing steels.

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INTRODUCTION

Hot-dip galvanizing is a widely used process for the protection of iron-based materials from corrosion. Coating characteristics such as corrosion resistance, thickness, appearance, and mechanical properties are primary parameters in this process. All of these parameters are influenced by the shape and thickness of the Fe-Zn alloy layers formed during galvanizing process. Chemical composition, geometrical shape, surface condition and dipping time of the parts to be galvanized and temperature of the zinc bath affect the formation of Fe-Zn alloy layers [1-15]. Silicon content higher than 0.03% in a steel is regarded critical since it leads to a reactive behavior that deteriorates the properties of hot-dip galvanized coating. This behavior is known as Sandelin Phenomenon [1], which changes the structure of the stable diffusion layers in the coating into another form composed of fine and discrete ζ crystals surrounded by η phase. The phenomenon causes an uncontrollable growth in hot-dip coating galvanizing coatings, which reach to a peak value at 0.08% Si as shown in the Sandelin Curve [1]. The fast growing ζ crystals leads to extremely thick coating layers, which cause over consumption of zinc and form brittle coatings with irregular thickness and poor surface characteristics.

In addition to the composition, surface properties of the steel also play an important role on the coating properties [5-8]. A prior forming process modifying surface topography subsequently may also alter the coating properties. Effect of the surface topography on the coating behavior can be explained by concave and convex surfaces produced on the steel in where the convex surfaces produce scattered alloy layers whereas the concave surfaces favor the growth of iron rich regions producing more compact and continuous layers [6].

To explain reactive behavior in hot-dip galvanizing coatings, a different theory has been proposed by Vazquez, which is called Reactive Zone Theory [15]. According to Vazquez, formation of subsurface oxide phases and heterogeneous presence of Si rich regions in hot rolled steel sheet affect the development of alloy layers during galvanizing. Presence of Si rich zones is considered to be effective on over growing of ζ phase. However, parameters controlling the formation of Si rich regions have not been clearly defined and the distribution of Si enriched regions requires further detailed analytical work to be carried out through extended surfaces.

Researchers have proposed various theories on the parameters affecting the coating characteristics [5-8, 15]. The complexity of the parameters which comprise surface roughness, deformed layers and silicon content in subsurface regions introduces difficulty in finding out a solution to the problem. In this study, these parameters were isolated from each other and the effect of each parameter on coating behavior was elucidated.

EXPERIMENTAL

Samples in size of 3 x 30 x 70 mm were cut off from hot rolled steel sheets with silicon contents associated with the Sandelin Curve, in where normal and reactive coatings can be encountered (Table 1).

Galvanizing experiments were carried out in a zinc bath at 450°C ±2°C. The zinc bath contained 0.03% Fe, which is the saturation level of iron at 450°C, 1.0% Pb to increase fluidity, and 0.010% Al to improve oxidation resistance.

Table 1. Chemical composition of the samples.

Sample	C	Si	Mn	P	S	Al
1	0.050	0.010	0.28	0.018	0.013	0.049
2	0.055	0.115	0.34	0.018	0.035	0.054
3	0.050	0.210	0.37	0.017	0.017	0.041
4	0.160	0.320	1.31	0.014	0.013	0.034

The samples were first cleaned with NaOH of 100 g/l at 70°C for 10 minutes and then pickled with HCl of 25 vol. % containing inhibitor Rodine 50 at room temperature for 10 minutes. Afterwards, a group of samples was ground with 60 grit SiC paper in order to generate a specific roughness. Other group was first ground with 240 grit SiC paper, and after a series of grinding process finally polished with 1µm diamond paste to obtain smooth polished surfaces with negligible deformation.

Surface topography of the conditioned samples was examined with Jeol 5600 JSM Scanning Electron Microscope (SEM) and surface roughness (Ra) of the surfaces was measured using Mitutoyo Surftest 301 Profilometer. For cross-sectional examinations, the surfaces were electrolytically plated with nickel to avoid edge rounding during metallographic sample preparation. The plated samples were metallographically prepared according to the method explained by Jordan et al [16], which employs a series of grinding and polishing steps and a final etching with 3% Nital solution (3 ml nitric acid and 97 ml ethanol).

Prior to galvanizing, the pickled, ground and polished samples were treated with flux containing 300gr/l $ZnCl_2.3NH_4Cl$ solution for 2 minutes at 60°C and dried in hot air flow at 125°C.

For galvanizing, the conditioned samples were immersed in the zinc bath for 10 minutes. Following galvanizing, the samples were quenched in water so for sure to examine only the Fe-Zn phases evolved in galvanizing process.

Thickness of the Fe-Zn phases was measured as a distance from η-ξ interface to the steel substrate, excluding the thickness of the outermost (η) phase, which included dross particles from the zinc bath.

RESULTS and DISCUSSION

The conditioned surfaces, and the cross-sections of the subsurface regions are as shown in Figure 1. The surface of the ground samples consist of valleys and ridges shaped by the SiC particles on the grinding papers. Additionally, slightly distorted layers were revealed on the cross-sections of the ground samples, in where the plastically deformed grains extended to the depth of 6 µm from the surface. Neither the pickled nor the polished surfaces obviously revealed any plastically deformed grains on the cross-sections. The pickled surfaces exhibited cavities on the surface, while the polished surfaces gave smooth planes with tiny abrasive traces. The roughness values of the mechanically formed surfaces were found considerably lower than that of pickled surface (Table 2)

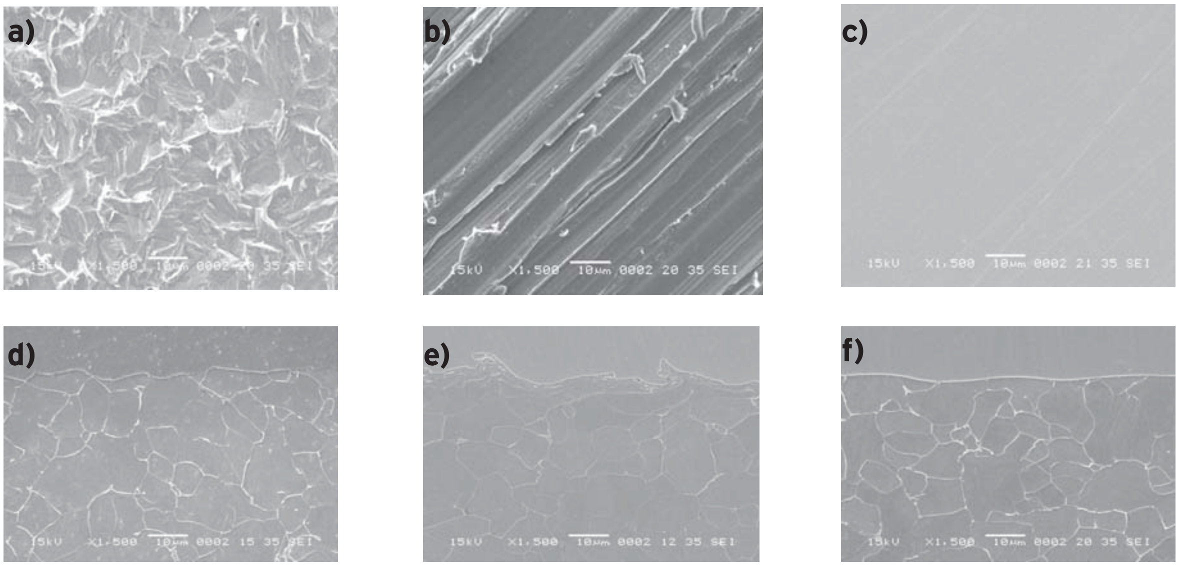

Figure 1. Surface topographies and cross-sections of the conditioned samples through SEM: pickled (a, d), ground (b, e), polished (c, f)

Table 2. Surface roughness of the conditioned samples.

Surface	Surface roughness, Ra (µm)
Pickled	2,21
Ground	0,80
Polished	0,02

Variation of the Fe-Zn alloy layer thickness of the pickled and the polished samples with respect to silicon content brings out the general shape of the Sandelin Curve with a peak at approximately 0.115%Si (Figure 2). Although this behavior agrees with the results of the previous studies [6-8], the ground samples without a peak in the Sandelin range exhibited a different curve than expected.

The pickled low Si containing steels produce a diffusion controlled homogeneous coating structure consisting of the phases of ζ, δ and Γ as expected (Figure 3).

The coating structures on the other pickled samples of higher silicon contents display similar characteristics of the Sandelin Curve.

The polished samples exhibit a significant reactive behavior even on the steel containing 0.010% Si, which has produced stable coatings with other treatments. In the polished sample, δ phase layers become thinner where ζ phase over grows due to the reactive behavior (Figure 4a). It is proposed that this enhanced reactive behavior is due to the exposure of silicon rich substrate layers after removing oxidized top surface layers by grinding and later on polishing. The steel containing 0.115% Si shows a distinguished reactive behavior producing a very thick coating which is mainly composed of large crystals of a well defined ζ and surrounding η phases (Figure 4b).

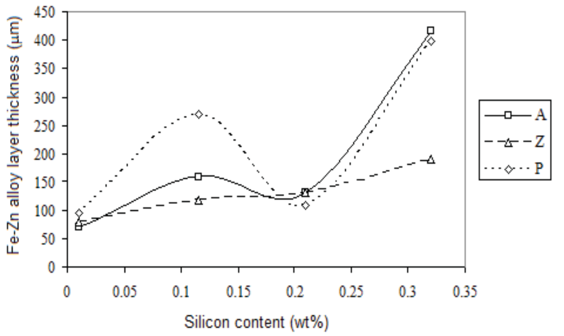

Figure 2. Variation of the Fe-Zn alloy layer thickness with silicon content as a function of the surface treatments: Pickling = A, Grinding = Z, Polishing = P

The grinding produces a thin and compact coating structure on the 0.010% Si containing steel, which is similar to the pickled one (Figure 4c). Compared to the others, the ground sample containing 0.320% Si yields a much thinner coating in this silicon concentration (Figure 4d).

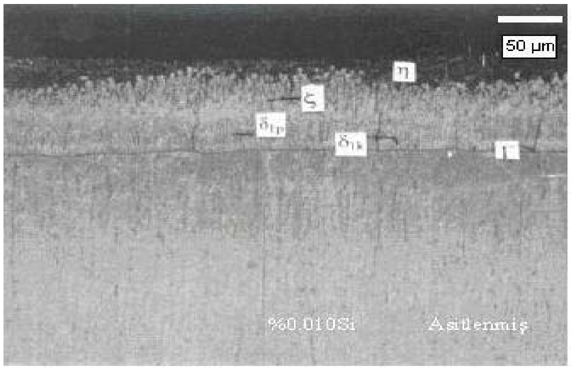

Figure 3. Effect of pickling on the coating structure of the steel containing 0.010 % Si.

It is seen that the surface characteristics developed by 60 grit SiC paper prevent an increase in the thicknesses of the coatings on account of Si content (Figure 5). The coatings generated on the ground samples with the 60 grit SiC paper having 270 µm SiC particles are consistent with those generated with shot blasting which has corundum particles in size of 100-200 µm [7], and grinding which has particles in size of 125-250 µm [8].

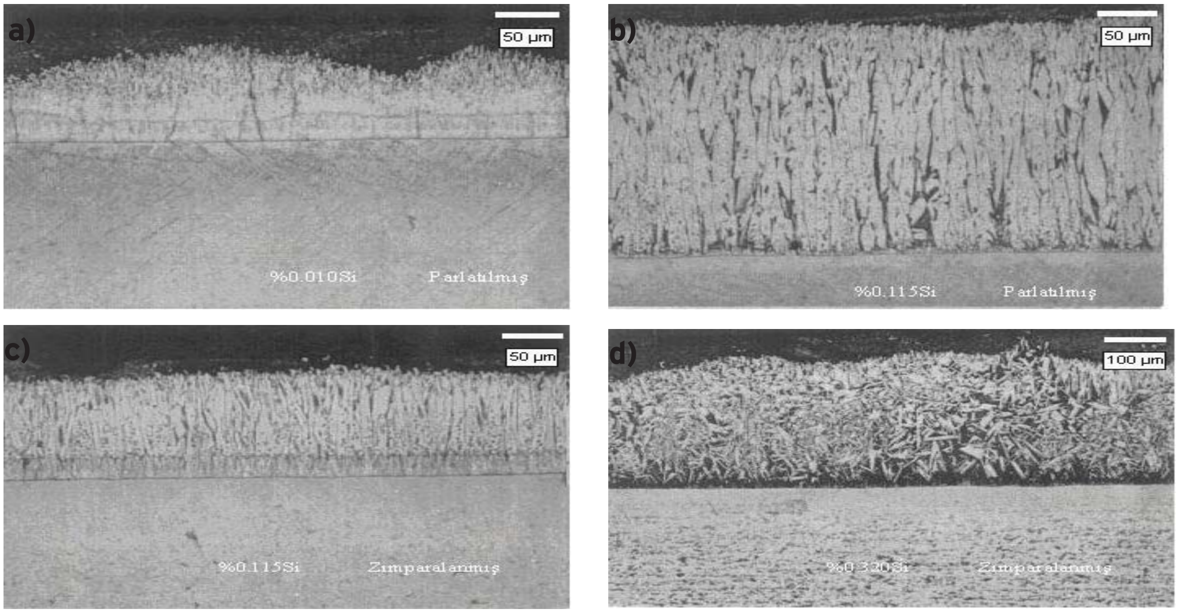

Figure 4. a) Effect of polishing on the coating structure of the steel containing 0.010 % Si. b) Effect of polishing on the coating structure of the steel containing 0.115 % Si. c) Effect of grinding on the coating structure of the steel containing 0.115 % Si. d) Effect of grinding on the coating structure of the steel containing 0.320 % Si.

The effect of surface topography on the reactivity can be explained by the model proposed by Bablik et al [6] on development of alloy layers on the concave and convex surfaces of silicon free steels. According to this model, the convex surfaces produce scattered alloy layers whereas the concave surfaces favor the growth of iron rich regions producing more compact and continuous layers. Thus, ζ phase crystals on the convex surfaces allow the liquid zinc to penetrate to the ζ-δ interface regions that cause the rapid growth of ζ crystals according to the following reaction:

$$\delta_{solid} + Zn_{liquid} \rightarrow \zeta_{solid} \qquad (1)$$

However, in the inward inclined surfaces, the Fe rich compact and continuous layers cause the reactions to be diffusion controlled. This explains the formation of stable coatings in the inward inclined surfaces of the galvanized pipes due to the blocking of zinc transfer and causing the reactions to be more of the diffusion controlled type [14].

In the present study, the pickled and polished samples with different surface topographies cannot produce Fe rich compact and continuous δ phase layers to inhibit the transfer of the liquid zinc in the more reactive regions. However, the samples ground with 60 grit SiC paper yield a characteristic surface topography to form stable Fe rich alloy layers with a dense Fe transfer from the concave surface of the valleys produced by the SiC particles.

CONCLUSIONS

Surface topography, i.e. the degree of surface roughness and the surface shape is the main factor controlling the stability of the hot-dip galvanizing coatings.

Therefore, a suitable surface topography for the steel products to be galvanized should be generated and measured with a reliable analytical method prior to galvanizing process. Compared with the previously obtained results, it can be suggested that intermediate roughness and sharp

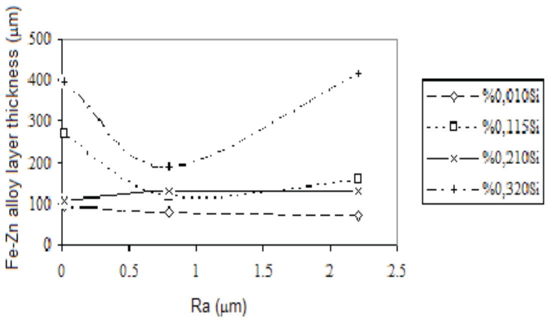

Figure 5. Variation of the Fe-Zn alloy layer thickness with surface roughness (Ra) as a function of silicon content in the ground samples.

asperities generated with abrasive particles having sizes in the range of 100-270µm can produce suitable galvanizing coatings on the steels having silicon contents in the Sandelin range.

REFERENCES

1. Sandelin, R. W. Galvanizing Characteristics of Different Types of Steels, Wire and Wire Products, 15 (1940), 655–676.
2. Horstmann, D. Hot Dip Galvanizing, Proc. 6th Int. Galvanizing Conf., Interlaken, Switzerland, 1961, pp. 319–328.
3. Pelerin, J., Hoffmann H., Leroy, V. The influence of silicon and phosphorous on the commercial galvanization of mild steels, Metall, 35 (9) (1981), 870–873.
4. Guttman, H., Niessen, P. Galvanizing of silicon steels in aluminum containing baths, Proc. Sem. On Galvanizing Silicon-containing Steels, Liege, Belgium, 1975, pp. 198–216.
5. Leroy, V., Emond, C., Cosse, P., Habraken, L. Study of the surface of silicon–killed steels in relation to hot–dip galvanizing, Proc. Sem. on Galvanizing Silicon-containing Steels, Liege, Belgium, 1975, pp. 97–119.
6. Bablik, H., Gotzl, F., Neu, E. Die Rauhigkeit verschiedener vorbehandelter Oberflächen und ihre Bedeutung für das Feuerverzinken. Z. Metalloberfläche, 9 (5) (1955), 69–71 (A).
7. Petter, F. Der Einfluβ einer mechanischen OberflächenVorbehandlung durch Strahlen auf das Verzinkungsverhalten siliziumhaltiger Stähle, Z. Metall, 30 (4) (1976), 339-342.
8. Hansel, G. Zum Einfluß der Topographie der Stahloberfläche auf die Ausbildung der Legierungsschichten bei der Feuerverzinkung, Z. Metalloberfläche, 38 (8) (1984), 347-351.
9. Heubner, U; Nilmen, F Hot Dip Galvanizing of Silicon Containing Steels: The Problem and Some Attempts at Its Solution, Werkst. Korros., 30 (3) (1979), 169–179.
10. Radtke, S. F. A New Method for Batch Galvanising of Silicon–Containing Steels, Metall, 34 (9) (1980), 865–867.
11. Dreulle, N. Galvanizing with Polygalva zinc alloy, Proc. 12th Int. Conf. on Hot–dip Galvanizing, Paris, France, 1979, pp. 186–191.
12. Allen, C. J., Battiston, L., Mills, R. J. Galvanizing plant trial using nickel–zinc process, CIM Bull., pp. 109–114.
13. Vazquez, A. J. Heat treatment and stabilization of the structure of galvanized coatings, Proc. 12th Int. Conf. on Hot–dip Galvanizing, Paris, France, 1979, pp. 147–155.
14. Vazquez, A. J., Damborenea, J. J. The Sandelin effect and continuously cast steels, Int. J. of Materials and Product Technology, 6 (1991), 175–216.
15. Vazquez, A. J. Galvanizing of silicon steels, reactive zone theory, Metall, 38 (1984), 952–955.
16. Jordan, C. E., Goggins, K. M., Benscoter, A. O., Marder, A. R. Metallographic preparation technique for hot–dip galvanized and galvannealed coatings on steel, Material Characterization, 31 (1993), 107–114.