Galvanizing of Silicon Containing Steels:
Effect of Mechanical Surface Treatments on Sandelin Phenomenon

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ABSTRACT

It is known that silicon contents of steels influence their galvanizing characteristics and cause galvanizing process to be a reactive type when silicon concentrations approach 0.8 wt-%. This effect was firstly observed by Sandelin, therefore is known as the Sandelin Phenomenon. Reactive type coatings create problems both on appearance and mechanical properties of the galvanized coatings and also cause an over coating on the steels, which increase the cost of galvanizing process. To avoid these problems, silicon contents of the steels to be galvanized are kept under the specified level of 0.03%. However, low silicon content causes several problems during continuous casting and similar reactive behaviour may appear when low silicon-containing steels are mechanically formed.

In this study, the influence of mechanical surface treatments on Sandelin Phenomenon was investigated. To determine any correlation between the surface parameters and the reactivity of galvanizing process, different surface topographies with/without deformed zones were produced on the surface of steel specimens varying silicon contents, by applying mechanical surface treatments such as grinding and polishing in addition to pickling which is a standardized practice in industrial galvanizing.

The coatings developed on the conditioned surfaces were examined through cross-sections with optical microscopy and SEM (Scanning Electron Microscopy).

The results showed that surface topography is the main factor controlling the stability of coating. Therefore, the surface topography of the steel to be galvanized should be correctly determined by reliable analytical techniques prior to galvanizing process.

Compared with the results previously obtained, it can be suggested that intermediate roughness and sharp asperities formed with abrasive particles in the size of 100-270 µm produce suitable galvanized coatings on steels varying silicon contents.

Key words: Hot-dip galvanizing, Sandelin Phenomenon, galvanizing of steels containing silicon, reactive steels

ÖZET

Silisyum içeriği %0.8'e yaklaştığında, çeliklerin silisyum içeriği bu çeliklerin galvanizleme karekteristiğini etkilemekte ve reaktif bir kaplamaya yol açmaktadır. Bu etki ilk kez Sandelin tarafından gözlendiğinden

Sandelin Olgusu olarak adlandırılmaktadır. Reaktif kaplamalar galvaniz kaplamaların görünümünde ve mekanik özelliklerinde problemlere yol açmakta ve ayrıca galvanizleme işleminin maliyeti yükseltecek şekilde çelik üzerinde aşırı kaplamaların oluşmasına yol açmaktadır. Bu problemden kaçınmak için galvanizlenecek çeliklerin silisyum içeriği %0.03'ün altında tutulur. Bununla birlikte, düşük silisyum içeriği sürekli dökümde problemlere yol açabilmekte ve düşük silisyum içerikli çelikler mekanik olarak biçimlendirildiklerinde benzeri reaktif davranış görülebilmektedir.

Bu çalışmada, mekanik yüzey işlemlerinin Sandelin Efekti üzerindeki etkisi incelenmiştir. Yüzey parametreleri ile galvanizleme işleminin reaktivitesi arasındaki ilişkiyi belirlemek için, değişik silisyum içeriğine sahip çelik numuneler üzerinde endüstriyel galvanizleme işleminde standart bir uygulama olan asitleme işlemine ilave olarak zımparalama ve parlatma gibi mekanik yüzey işlemleri uygulayarak deformasyonlu/deformasyonsuz farklı yüzey topografileri yaratılmıştır.

Değiştirilmiş yüzeyler üzerinde gelişen kaplamalar ışık ve taramalı electron mikroskopları ile kesitleri boyunca incelenmiştir.

Sonuçlar, kaplama stabilitesini kontrol eden ana faktörün yüzey topografisi olduğunu göstermiştir. Bu yüzden, kaplanacak çeliğin yüzey topografisi güvenilir analiz cihazları kullanılarak doğru bir şekilde belirlenmelidir.

Önceden elde edilen sonuçlarla kıyaslandığında, 100-270 μm boyutundaki aşındırıcı partiküllerle oluşturulan orta derecedeki yüzey pürüzlülüğünün ve keskin yüzey özelliklerinin farklı silisyum içeriğine sahip çeliklerde uygun kaplamalar oluşturacağı belirtilebilir.

Anahtar kelimeler: Galvanizleme, Sandelin Olgusu, silisyum içeren çeliklerin galvanizlenmesi, reaktif çelikler

1. INTRODUCTION

Hot-dip galvanizing is a widely used process for protection of iron-based materials from corrosion. Coating characteristics such as corrosion resistance, thickness, appearance and mechanical properties are primary parameters in this process. These parameters are affected by the shape and thickness of the Fe-Zn alloy layers formed during galvanizing process considerably. Chemical composition, geometrical shape, surface condition and dipping time of the parts to be galvanized; composition and temperature of the zinc bath affect the formation of Fe-Zn alloy layers[1-15].

When silicon content of the steel is critical such as higher than 0.03%, it exhibits a reactive behaviour that deteriorates the properties of the galvanized coating. This behaviour is known as Sandelin Phenomenon [1], which changes the structure of the stable diffusion layers in the coating into another form that consists of fine and discrete ζ crystals surrounded by η phase. This behaviour causes an uncontrolled growth in the coating layers which reach to a peak value at 0.08% Si as can be seen 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 steel also play an important role on the properties of the coating [5,6,7,8]. The mechanical shaping of steel may also alters surface characteristics which later affects the properties of the coating.

Various explanations were proposed about how the above parameters influence the coating characteristics [5,6,7,8]. The complexity of the parameters which comprise surface roughness, deformed layers and silicon content in the subsurface regions presented difficulty in bringing a solution to the problem. In this study, these parameters were isolated from each other and the effect of each parameter on coating behaviour was attempted to be explained separately.

2. EXPERIMENTAL TECHNIQUE

Samples were cut off from the steel sheets, which were produced by hot rolling process. The steels were selected to have a certain range of silicon content which corresponded to those specified in the Sandelin Curve as the compositions at which the normal and reactive coating behaviours were exhibited (Table 1). The dimensions of the samples used in the galvanizing experiments were specified as 3x30x70mm.

Table 1. Chemical composition of the steels

Sample No	Chemical Composition (wt-%)					
	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	0.074
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 temperature of zinc bath was kept at 450°C±2°C. Zinc bath contained 0.03% Fe, which is a saturation level at 450°C, 1% Pb to increase fluidity and 0.01% Al to improve oxidation resistance.

Samples were treated first with NaOH of 100 g/l at 70°C for 10 minutes and with HCl of 25 vol-% containing inhibitor Rodine 50 at room temperature for 10 minutes to produce suitable clean surfaces before galvanizing process.

Having treated with alkali and acid solutions, samples were wet ground with 60 grit SiC paper in order to form surfaces in a certain degree of roughness. Other samples were ground with 240 grit SiC paper and finally polished with 1μm diamond paste to obtain smooth polished surfaces with negligible deformation

Surface topography of the samples was examined with Jeol 5600 JSM Scanning Electron Microscope (SEM) and surface roughness (Ra) of the treated surfaces was measured using Mitutoyo Surftest 301 Profilometer.

For cross-sectional examination of the subsurface regions, conditioned surfaces were electrolytically coated with nickel, polished and finally etched with Nital 3.

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

Galvanizing experiments was carried out dipping the samples into the zinc bath for 10 minutes. After dipping, samples were quenched with water so as to examine the Fe-Zn phases developed solely during galvanizing.

Coated samples were prepared according to the method explained by Jordan et al [16] and examined with optical microscope and SEM.

Coating thickness was defined by measuring the distance of the η-ξ interface in coating to the substrate, excluding the thickness of the outermost (η) phase which included dross particles stuck from the zinc bath.

Fe-Zn phases were identified with semi-quantitative SEM-EDS analysis performed over the cross-sections of the coatings.

3. EXPERIMENTAL RESULTS

The conditioned surfaces and the cross-sections of the subsurface regions are shown in Figure 1. The ground surfaces consisted of valleys and ridges formed by the SiC particles on grinding paper. Additionally, some distorted layers were revealed on the cross-sections in which plastically deformed grains extended to the depth of 6 μm from the surface. Neither the pickled nor polished surfaces obviously revealed any plastically deformed regions in cross-sections. The pickled surfaces exhibited cavities on the surface, while the polished surfaces gave smooth planes with tiny abrasive traces.

Roughness values of mechanically formed surfaces were considerably lower than that of pickled surfaces (Table 2).

Table 2. Surface roughness of the formed surfaces

Formed surface	Ra (μm)
Pickled	2.21
Ground	0.80
Polished	0.02

It is observed that the variation of the coating thickness of pickled and polished samples with silicon content gave the general shape of Sandelin Curve with a peak at approximately 0.115%Si (Figure 2). This behaviour was found to be agreeing with the results presented in the previous studies [6, 7, 8]. On the contrary, ground samples with no significant peak in the Sandelin range exhibited different curve than the expected.

The pickled low Si containing steels produced a diffusion controlled homogeneous coating structure consisting of the phases of ζ, δ ve Γ as expected (Figure 3). Coating structures obtained in other acid treated samples showed similarity with those of the characteristic Sandelin Curve.

The polished samples caused more reactive behaviour even with the steels containing 0.010% Si which formed stable coatings with other treatments. In this sample, δ phase layers became thinner where ζ phase over grew due to reactive behaviour the (Figure 4) It was thought that this enhanced reactive behaviour was due to the reactive layers of silicon rich that exposed after removing the top layers of substrate. The steel containing 0.115% Si showed a distinguished reactive behaviour producing a very thick coating which was mainly composed of large crystals of a well defined ζ and surrounding η phases (Figure 5).

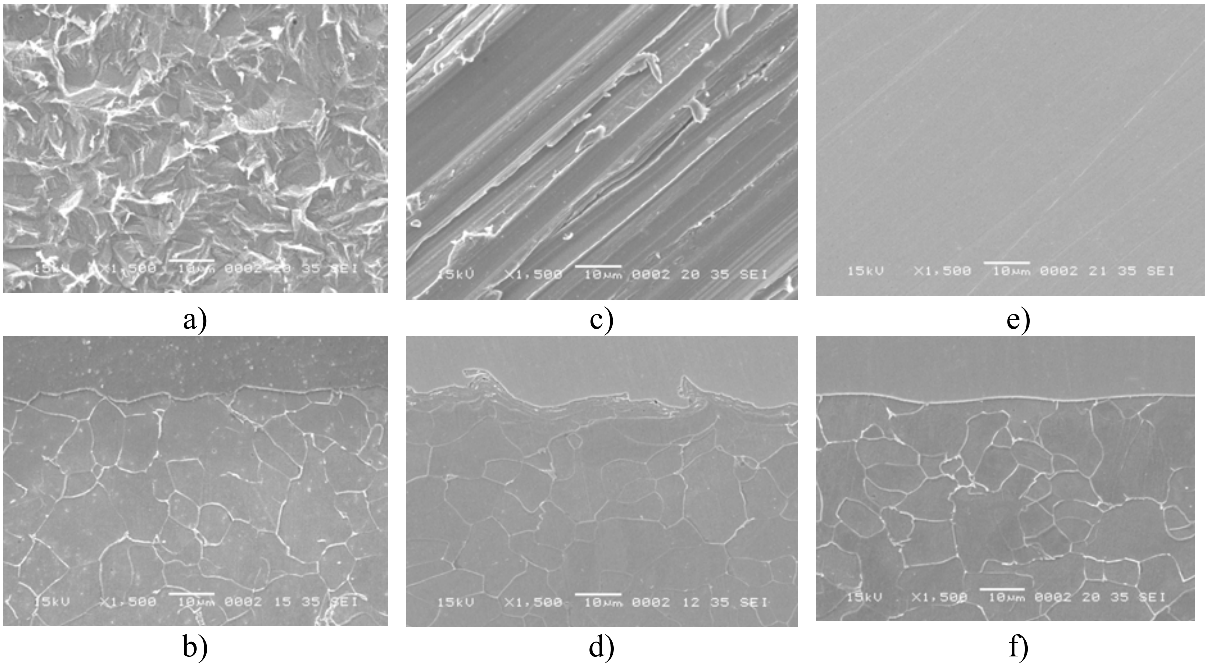

Figure 1. Surfaces and cross-sections through SEM: pickled (a, b), ground (c, d), polished (e,f)

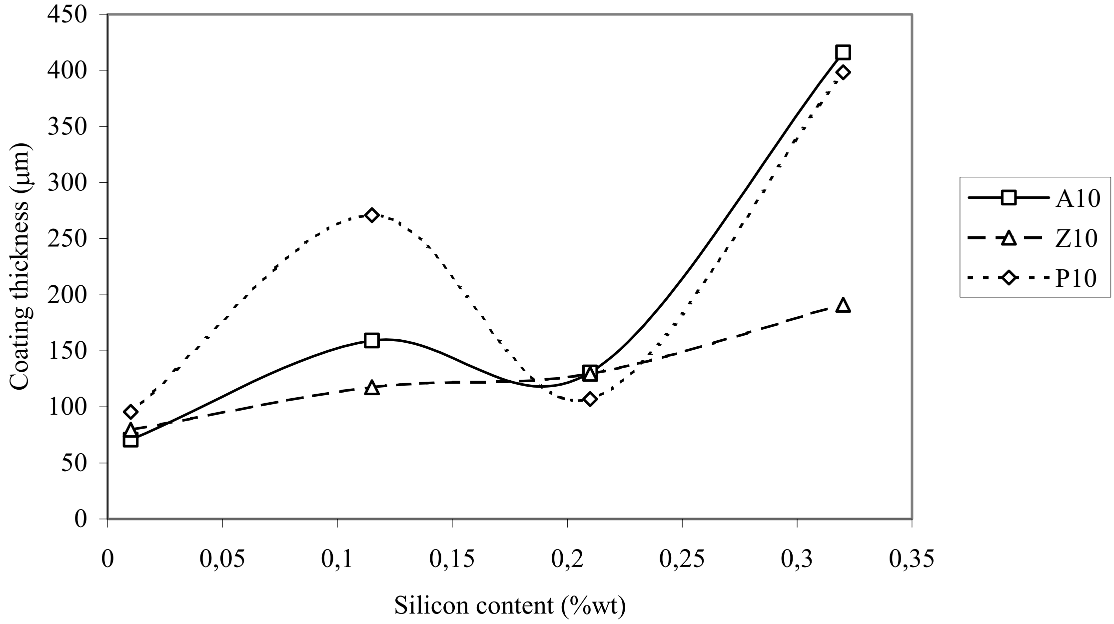

Figure 2. Variation of coating thickness with silicon content as a function of performed surface treatment A = pickling, Z = grinding, P = polishing and 10 = dipping time of 10 min

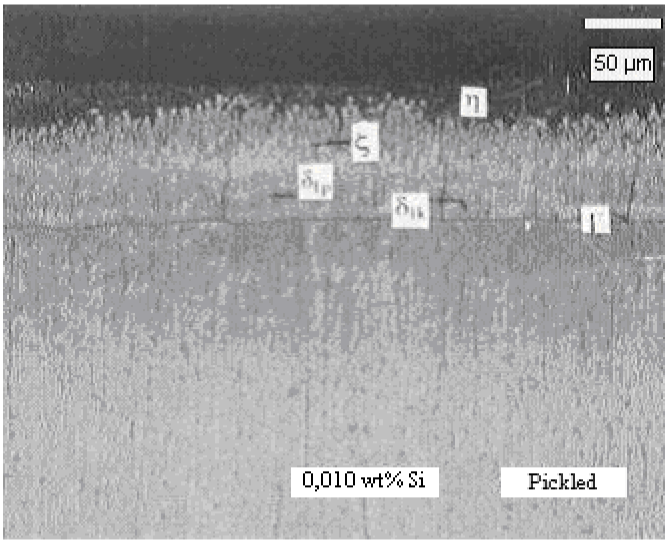

Figure 3. Effect of pickling in steel containing 0,010 wt% Si on coating morphology

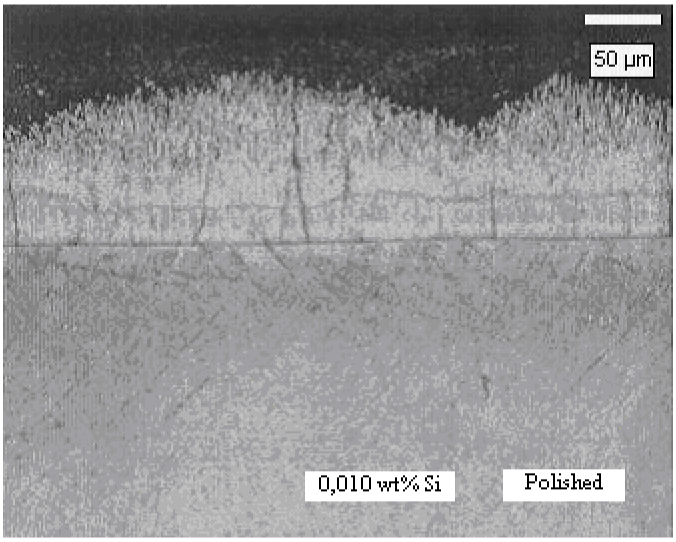

Figure 4. Effect of polishing in steel containing 0,010 wt% Si on coating morphology

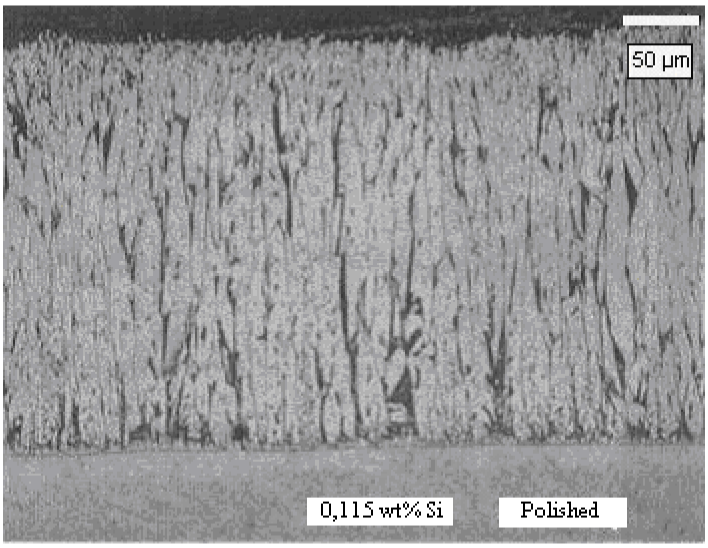

Figure 5. Effect of polishing in steel containing 0,115 wt% Si on coating morphology

Grinding produced thin and compact coating structure for the 0,010%Si containing steel, which was similar to that obtained with pickling (Figure 6). The ground sample containing 0.320%Si yielded thinner coating in this silicon concentration (Figure 7).

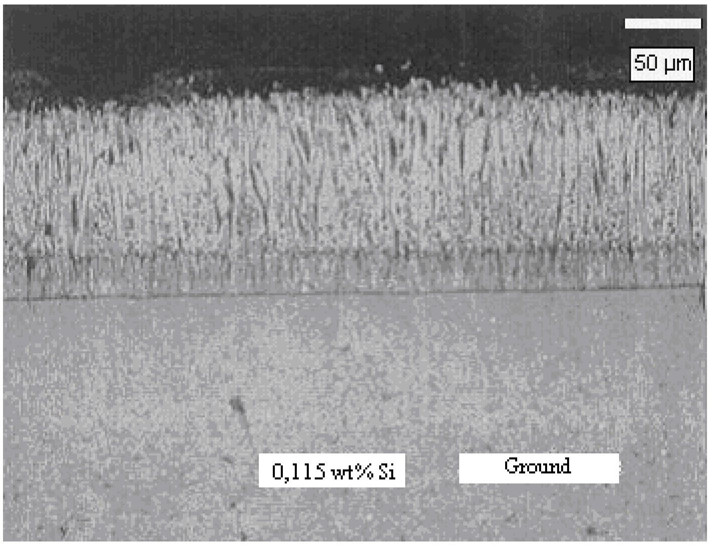

Figure 6. Effect of grinding in steel containing 0,115 wt% Si on coating morphology

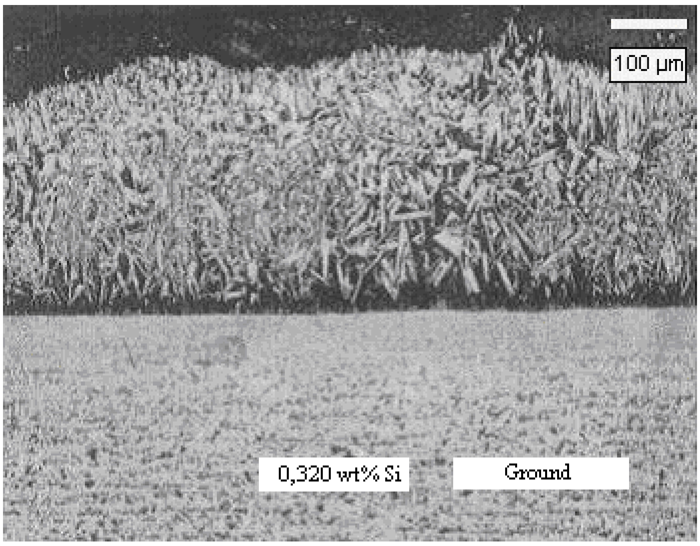

Figure 7. Effect of grinding in steel containing 0,320 wt% Si on coating morphology

It was found out that the surface characteristics developed by 60 grit SiC paper prevented an additional increase in the thicknesses of coatings because of silicon (Figure 8). The coatings obtained with 60 grit SiC paper including SiC particles in size of 270 µm were consistent with those obtained by Peter [7] with shot blasting using corundum in size of 100-200µm and by Hansel [8] with shot blasting using corundum in size of 125-250 µm.

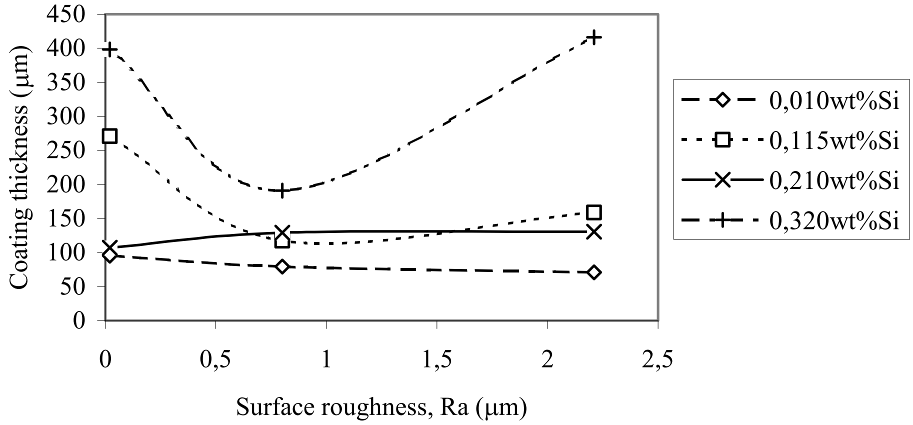

Figure 8. Variation of coating thickness with surface roughness (Ra) as a function of silicon content

In this study, the pickled and polished samples both without deformation produced reactive behaviour in Sandelin region. Even polished sample with the lowest silicon content resulted in a reactive coating. However, the ground samples containing deformed layers prevented the reactive behaviour to form. Therefore, it could be proposed that surface topography formed by various treatments was the main parameter controlling the stability of coating.

4. DISCUSSION

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 favoure 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 :

$$\delta_s + Zn_l \rightarrow \zeta_s \quad (1)$$

In the inward inclined surfaces however, 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 present study, the pickled and polished samples with varying surface topographies can not produce Fe rich compact and continuous δ phase layers to inhibit the transfer of the liquid zinc in the more reactive regions. The samples ground with 60 grit SiC paper, however, produce 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 .

To explain reactive behaviour in galvanized 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 done through extended surfaces.

5. CONCLUSION

Surface topography, i.e. the degree of surface roughness and the surface shape is the main factor controlling the stability of coating. Therefore, the surface topography of the steel to be galvanized should be correctly determined by reliable analytical techniques prior to galvanizing process.

Compared with the results previously obtained, it can be suggested that intermediate roughness and sharp asperities formed by abrasive particles in the size of 100-270µm can produce suitable galvanized coatings on steels varying silicon contents.

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