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Short Period Phosphating of Cold Rolled Steel

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Short period phosphating (of about one minute duration) on differently treated cold rolled steel surfaces highlighted the growth of the first-stage phosphate crystals. The surface topography affected the nucleation of the phosphate crystal and its subsequent growth. This was revealed by the scanning electron microscope. The shear strength of the phosphate crystal deposited on the steel substrate were measured to be 850 kN.m^{-2} for the first-stage and 450 kN.m^{-2} for the second-stage.

INTRODUCTION

The use of zinc phosphate coating for the protection of steel surface is well documented.¹⁻⁴ Phosphate crystal deposition requires a nucleation site where the primary phosphate crystal growth proceeds vertically and this is followed by dendritic growth in the second-stage. However, the nature of the two-stage primary and secondary growth of these phosphate crystal remains complex and is not fully understood.⁵ It is generally accepted that the primary nucleation of phosphate crystals is instantaneous and their growth proceeds *via* an addition mechanism. The phosphate crystals become detectable after reaching a critical size.

The ensuing second-stage dendritic phosphate crystal growth results from active sites on the rough and irregular primary crystal layer. Hence the protection of a cold rolled steel (CRS) surface by the phosphate crystal depends essentially on the initial nucleation in the first-stage. A good protective layer is derived from an even nucleation of these densely packed phosphate crystallites, distributed uniformly across the surface of the steel substrate.

Most metal surfaces are irregular; any points or sites that protrude out of the substrate surface would exhibit a high surface activity. Interaction with these active sites will enhance the rate of zinc phosphate crystal nucleation, growth and deposition.⁶ Surface treatment of metal substrate will alter its surface topography and/or oxide morphology which will influence the phosphate crystal growth. These active sites are related to the degree of the surface heterogeneities. An increase in these active sites by surface treatment would encourage a dense and uniform phosphate crystal growth resulting in a durable phosphate coating. This paper is an extension of our previous investigation on the phosphating of cold rolled steel (CRS).⁷ The coating, its weight and its tensile shear strength are reported whilst the focus of the paper is on surface topography and effect of short-time phosphating. Influence on the rate of phosphate nucleation, growth and adhesion on differently treated cold rolled steel are also discussed.

EXPERIMENTAL

The cold rolled steel panels of dimension $10.2 \times 2.5 \times 0.1$ cm were first degreased with toluene and acetone. They were then immersed in a hot 5% trisodium phosphate/1% Teepol solution which was maintained at 80°C for a duration of 10 minutes. This was followed by a rinse with warm distilled water and these 'cleaned' panels were conditioned at 90°C for 5 minutes. These were then stored in a desiccator.

The degreased/alkaline washed steel panels were then subjected to different surface treatments prior to phosphating by immersion. These differently treated CRS panels were weighed after surface treatment and reweighed after being phosphatized for a short period at 75°C. Phosphatized panels were rinsed with distilled water and conditioned in an oven at 90°C for 24 hours. The scanning electron microscopy examinations of these CRS surfaces were carried out with a Jeol 35 CF electron microscope.

The shear strengths of the treated CRS surfaces bonded to single pack silicone sealant before and after phosphating were measured in a simple lap-shear joint as in the previous work.⁷ The joints, 2.5 cm wide, had an overlap of 2.0 cm and a glue-line thickness of 0.1 mm. The cured joints were sheared by an Instron 1026 tensile machine at a strain rate of 7 mm/minute.

RESULTS

The scanning electron microscope is an indispensable tool for the evaluation of zinc phosphate crystal structure on differently treated cold rolled steel surfaces. Details of the metal surface characteristics were examined at a magnification of 5000. Electron micrographs presented in a previous report⁷ revealed the different topographies of these differently treated CRS surfaces. The distinctive topographic features were observed for the heated (oxidized), dilute hydrochloric acid etched and the acid etched/boiled samples.

Figures 1 to 3 show the growth of zinc phosphate crystals up to 60 seconds on these treated CRS surfaces. These phosphate crystals are either in platelet or disc-like form. The platelet structure (Fig. 2b) was usually coarse and thicker than the disc-like structure (Fig. 3b).



FIGURE 1 Electronmicrographs of short-time phosphating on degreased/alkaline washed CRS. (a) Platelet and disc-like phosphate crystals completely covering the CRS surface after 30 sec. phosphating. (b) Phosphate crystals thickening and the layer becoming more dense after 60 sec. phosphating.



FIGURE 2 Electronmicrographs of short-time phosphating on CRS etched with dilute hydrochloric acid. (a) The nucleation/growth of the first stage primary phosphate crystal is slow and continuous after 30 sec. phosphating. (b) The deposition of the platelet crystal after 60 sec.

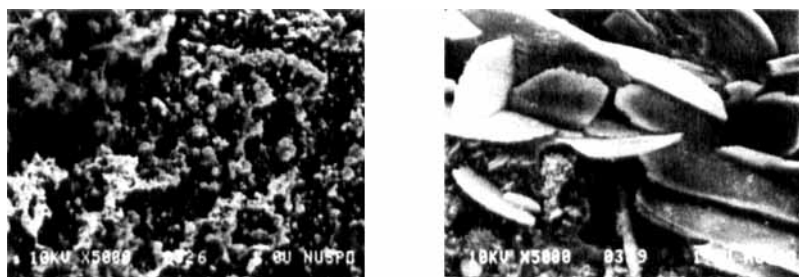


FIGURE 3 Electronmicrographs of short-time phosphating on CRS etched in dilute hydrochloric acid and subsequently boiled in water. (a) The first stage phosphate crystal growth occurring at isolated active sites after 30 sec. phosphating. (b) The disc-like phosphate crystals spreading over the primary phosphate layer after 60 sec. phosphating.

The degreased/alkaline washed CRS surface seemed to have activated the surface oxide (α -FeOOH) to allow phosphate crystal deposition within the first few minutes (Fig. 1). The dilute hydrochloric acid treatment smoothed the metal surface irregularities, enhanced the active centres by exposing the grain boundaries and etch pits to provide a slow and continuous growth of phosphate crystal layer. The nucleation of zinc phosphate crystals on acid etched/boiled surface began at isolated active centres (Fig. 3a). These phosphate crystals grew laterally from the primary phosphate layer and resulted in a non-uniform layer.

These results indicated that in the case of phosphating by immersion, the phosphate crystal was attained through two stages of growth. With progress in time, these crystals increased in size and weight at various rates to cover the CRS surfaces. The phosphate coating deposited was monitored by measuring its weight deposited per unit time. Figure 4 shows a rapid phosphate crystal nucleation/growth at the beginning of the phosphating process. The first-stage phosphate growth seemed to have completed within the first minute, except for the degreased/alkaline washed and the dilute hydrochloric acid etched CRS surfaces. For the dilute hydrochloric acid etched surface, saturation was observed after 3 minutes. This lengthening of the first-stage nucleation/growth could be attributed to the presence of significantly more active sites. Therefore in general, the primary saturation stage occurred within the first few minutes of phosphating, and the coating weight deposited was approximately $4 \text{ g.m}^{-2} \text{ min}^{-1}$ in all cases and $8 \text{ g.m}^{-2} \text{ min}^{-1}$ for the acid etched surface.

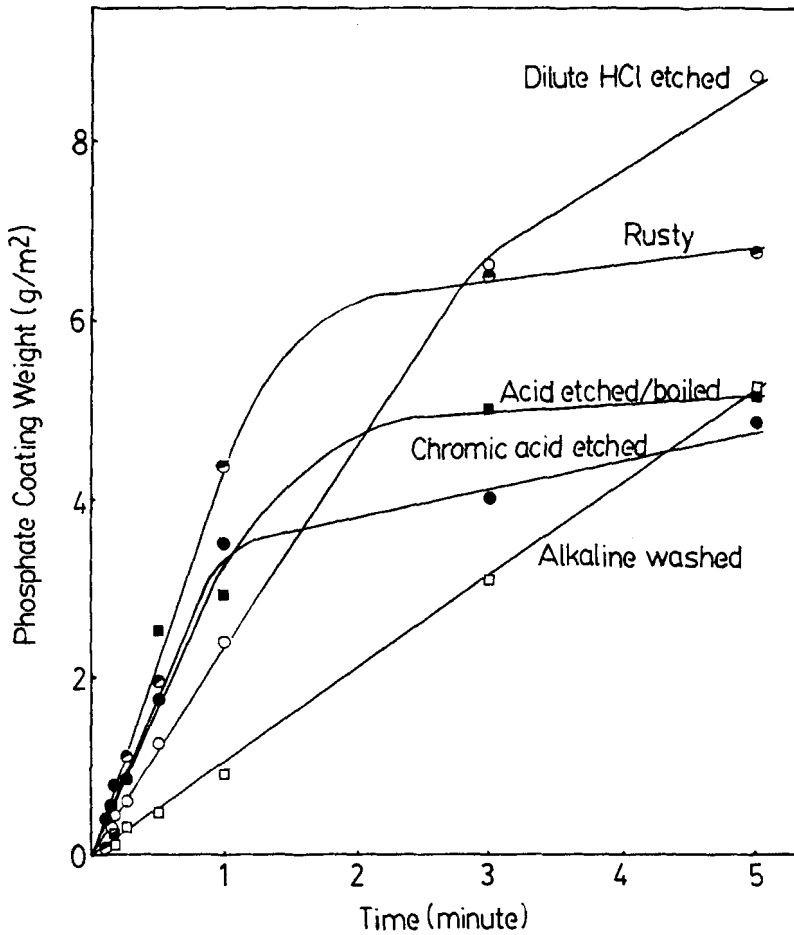


FIGURE 4 Rate of short-time phosphating on treated CRS.

The results of the short-time phosphating added a valuable dimension to our previous report.⁷ As little information on short-time phosphating behaviour was then available, approximate plots which increase monotonically were assumed for phosphating. With the information on short-time phosphating, this has enabled us to combine some of our previous results in a more accurate plot covering both short and long period phosphating (Figure 5). Two-stage phosphate deposition was observed for these differently treated CRS surfaces. Upon com-

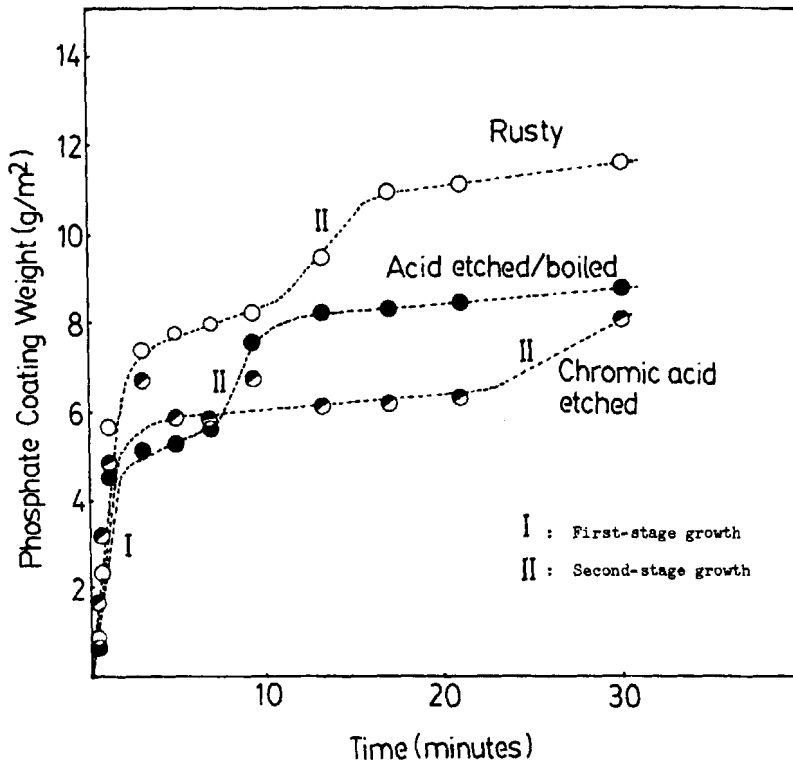


FIGURE 5 Kinetics of phosphating treated CRS surfaces.

pletion of the first-stage growth, a second-stage dendritic phosphate formed as manifested in the pronounced kink in these curves. However, given the paucity of data, it was not possible at this stage to determine precisely where the first-stage ended and where the second-stage began. Further investigation into the kinetics of phosphating is under way and it may throw more light on the matter.

Table 1 shows the results of the first and second stage phosphate deposition on differently treated CRS surfaces. The primary phosphate deposition varies from 1.05 to $4.30 \text{ g m}^{-2} \text{ min}^{-1}$ for different surfaces. The reproducibility of these data as compared to those obtained previously is reasonably good. However, from computation it was found that a significant difference in the deposition rate between the primary and secondary growth stage was observed. It appeared that this low secondary phosphate deposition rate may be due to an effect caused

by the concentration gradient and/or a different mechanism for secondary phosphate deposition.

TABLE I
Rate of primary and secondary phosphate deposition on treated CRS

Surface treatment	This paper First-stage (primary) g/m ² min.	Recalculated results from previous paper ⁷	
		first-stage (primary) g/m ² min.	second-stage (secondary) g/m ² min.
Degreased/ alkaline washed	1.05	1.06	0.06
Dilute HCl etched	2.30	3.80	0.13
Dilute HCl etched/boiled	3.25	3.30	0.71
3% Chromic acid etched	3.50	2.50	0.18
Rusty	4.30	5.45	0.50

To investigate this dual-stage crystal growth phenomenon further, the adhesion of these layers was studied using the silicone/metal lap joint composite method. The shear strengths are presented in Figure 6. The graphs show the variation of shear strength of the bonded composites with the time of phosphating. Adhesive failure prevailed in all non-phosphated composites. However, failure within the phosphate layer was observed for all phosphated surfaces.

It is interesting to note that for the dilute hydrochloric acid etched and the acid etched/boiled panels, an improvement in the shear strength of the composite was obtained for short-time phosphating. The highest attainable shear strengths was measured as 850–900 kN.m⁻². This significant increase may reflect an improved interfacial adhesion in this case. Consequently this primary phosphate layer may provide the phosphated CRS surface with better penetration or keying for bonding using the silicone, hence the high joint strength. With increase of phosphating time, the second-stage dendritic crystal growth would intertwine and result in a weaker shear strength. The shear strength of the second-stage phosphate crystal layer was about 400–500 kN.m⁻². This value was consistent with that reported by us earlier⁷.

DISCUSSION

Scanning electron microscopy has provided further insight in the nature

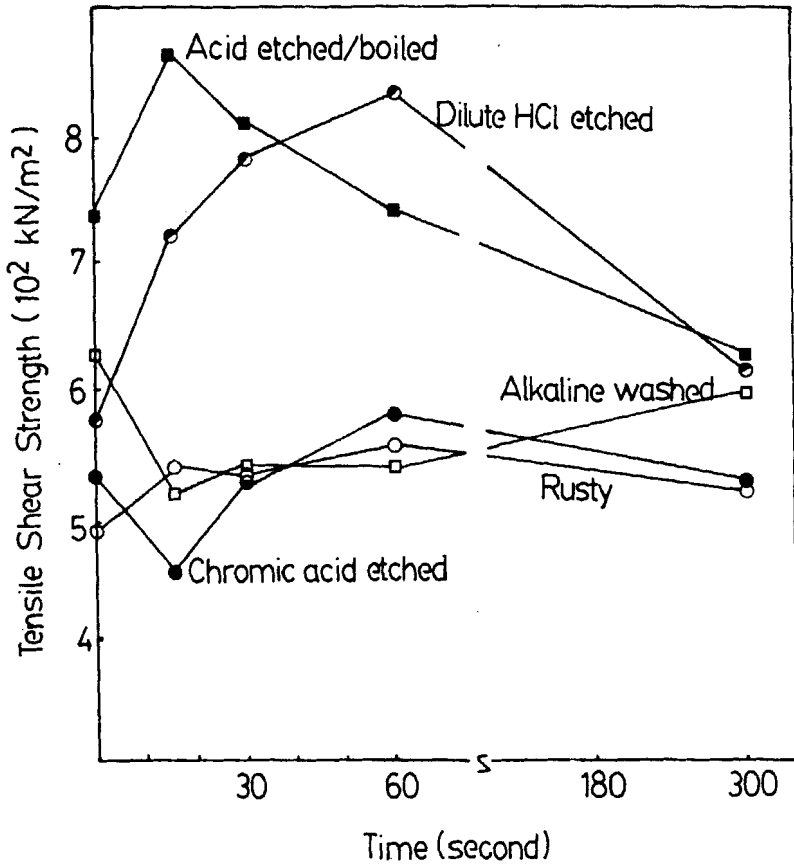


FIGURE 6 Effect of phosphating time on the shear strength of treated CRS/silicone joints.

of phosphate crystal layers, particularly those formed during the initial period of phosphating.

Surface topography and surface oxide (or hydrated oxide) morphology of cold rolled steel were modified by various surface treatment prior to phosphating in order to provide a better substrate surface for coating deposition. The rate and the nature of phosphate nucleation/growth on a heterogeneous surface would be expected to be influenced by the number or distribution of active sites present. However, interaction at these active sites is still not well understood.

Phosphating of the steel surface is seen as a two-stage process where

the primary nucleation of phosphate begins at the active sites. On its completion it provides secondary sites for further growth. The first-stage is a rapid nucleation at the active sites with immediate growth of the primary phosphate crystal, which reaches a detectable size within the first minute of phosphating. The primary phosphate nucleation/growth will reach a steady-state when the rate of deposition becomes constant. This dynamic equilibrium may be established between the crystals and the phosphate solution. After a while, the secondary dendritic phosphate growth follows. The low rate of the secondary phosphate crystal deposited found for all surfaces could be due to the concentration gradient at the interface.

The results also demonstrated that in the case of the dilute hydrochloric acid treated CRS, the phosphate crystal nucleation/growth results in a complete and dense coverage of CRS surface. A high weight secondary phosphate deposition may follow in this case. The action of this acid was to smoothen the CRS surface by exposing further grain boundaries and etch pits thus increasing the number of active sites for crystal growth. This topographic feature would encourage a more uniform primary nucleation/growth, and favour the subsequent second-stage phosphate deposition.

Dilute acid etch/boil treatment may inactivate the surface oxide layer and also alter its morphology. This inactivation may result in a sparing coverage of the surface during the first stage. This effect is more geometrical than chemical in nature. Furthermore, the phosphate crystal orientation at both the primary and secondary nucleation sites could influence the structure of the subsequent coating deposited. In fact, information concerning the type of phosphate crystal structure provides a better understanding of the durability of industrial phosphate coating on CRS, its shear strength and failure pattern.

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