

Note

Studies on defects in galvanized coating on steel wire

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Causes for deposition of defective galvanized coating (lumpy deposition of coating during hot dip galvanizing) of carbon-steel wire have been investigated. It is established that the lumpy deposition is caused due to segregation of silicon on the surface of steel wire. Due to this change in composition of the steel at surface, the regions get modified and lie in Sandelin hyper reactive zone. This accelerates reaction of steel with molten zinc in those localized regions of the surface and leads to formation of lumpy deposition of zinc. Scanning electron microscopy, energy dispersive X- ray analysis and Raman spectroscopy of lumpy wire (LW) and normal wire (NW) coatings confirm the presence of silicon bearing phases present in the LW coating. It is observed that due to localized high concentration of silicon on steel surface, a diffused and porous zeta layer instead of normal compact delta and zeta layers is formed. Thus, incoherent deposition of zinc layers occurs on steel surface. In order to control this problem, it is suggested to maintain silicon equivalent in the steel below 0.04 wt% and conduct flash pickling of wires in oxidizing acid to dissolve silicon rich phases.

Keywords: Galvanized coating, Lumpy deposition, Raman spectroscopy, Sandelin effect, Steel wire

Steel wires are galvanized after pre- treatments such as lead bath patenting, pickling, rinsing, fluxing, drying and finally galvanizing in molten zinc bath maintained at $450 \pm 5^\circ\text{C}$. They are then cold drawn to different degree of reductions using solid and liquid lubricants. Due to good ductile property and softness of zinc metal it flows with steel during drawing of wire. Normally zinc coating accommodates compressive stresses easily without any peeling off¹. It is reported that zinc coating on steel acts as solid lubricant during the drawing operation². Many researchers in the past have investigated the type of coating on forming limit strains, strain distribution, interface friction coefficient variation, lubrication characteristics, surface roughening and wear behaviour during forming operations³⁻⁵. Vagge *et al.*⁶

have shown that a linear relationship exists between the strain and the degree of delamination of zinc coating. Presence of MnO (manganese oxide) formed during annealing of steel substrate prior to galvanizing is attributed as one of the causes of delamination of coating during forming⁷⁻¹⁰. These studies pertain delamination of zinc coating either at inter metallic layer (IML) or cracking in the body of coating itself. In wire drawing industries where galvanized wire is drawn to different degree of reduction, a peculiar problem of “shaving” of zinc coating is reported by many industries. It is certainly due to unevenness of the galvanized surface. However, the exact reason for this unevenness has never been reported. Literature survey reveals that no studies to explain this phenomenon and to suggest remedial measures have been published so far. It is a common problem and a matter of great concern to the rope manufacturers who draw the wire after galvanizing. The present study was therefore undertaken to address this problem and identify the causes for it using different analytical techniques. The scientific explanations of results and possible remedial measures are reported.

Experimental Procedure

The experiments were performed by taking two types of wire, namely (i) the wire which did not exhibit any shaving problem, abbreviated as normal wire (NW); and (ii) the wire having the problem of shaving, abbreviated as lumpy wire (LW). The galvanized wire samples of 7 mm diameter with and without lumpy coating were collected from the manufacturing line of the company. The cross-sections of the two types of wires (lumpy and normal) were mounted in resin, mechanically polished and etched in Nital solution (2.5% nitric acid dissolved in ethanol). The chemical composition of the substrate steel and the coating was determined using energy dispersive X- Ray analysis (EDXA). Surface topography and EDX analysis were performed by using Jeol scanning electron microscope (JSM 840A). Raman spectroscopy of NW and LW samples was performed using Alpha Dispersive Raman Spectroscopy, exciting laser beam of He-Ne laser of 532 nm wavelength on the samples. The power of

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laser was kept lowest possible (6 mw) to avoid transformation of phases, if any, due to heating effect. The desired regions on the surface of the specimens to be studied were focused through an Olympus microscope at $\times 50$. The sample holder was attached to motorized platform with Jokey to facilitate fine focusing and mapping over a suitable desired portion of the specimens. The grating was 672 lines/mm and the pinhole was 25 μm . Prior to analysis of the samples, the instrument was calibrated by using pure silicon at the peak of 522 cm^{-1} .

Results and Discussion

Since the problem of shaving of the coating was caused due to lumpy deposition of zinc during the process of galvanizing, efforts were made to ascertain the causes of lump formation by examining the microstructures of coatings of lumpy wire (LW) and normal wire (NW). The morphologies of zinc coating on the two types of wire are shown in Figures 1(a) and (b). It is evident from Fig. 1 (a) that NW coating exhibits normal stratified Fe-Zn alloy layered microstructure with distinct phases of intermetallics. In case of LW coating, however, no distinct structure is revealed [Figure 1(b)]. In this case, small crystallites, haphazardly distributed, all over the coating are evident. The chemical analysis of these phases reveals the presence of Si, Fe, P and Zn (Table 1). For the sake of comparison, chemical analysis of NW coating is also included in this table. It is seen from the data of this table that chemistry of the LW coating is entirely different from that of the NW coating. The steel and zinc interface in the LW coating shows 4.89 wt% of iron and 2.26 wt% of silicon. Iron content of about 5% in zinc-iron intermetallics corresponds to zeta phase (ξ), with chemical formula of FeZn_{13} . This indicates that in the LW coating, the zeta phase has shifted up to the steel-coating interface.

The data of Table 1 further reveal that content of silicon in the LW coating at its interface as well as away from it at points 2 and 3 [Fig. 1(b)] is abnormally high. In the top layer of this coating, iron content is 3.62 wt% which is in range of iron content

of the ξ phase. This suggests that the top layer is also transformed into zeta phase. The silicon content is also very high in this layer. The presence of abnormally higher content of silicon at the interface as well as in the top layer of the LW coating indicates that this element plays important role in formation of the lump. The phosphorus content in different layers

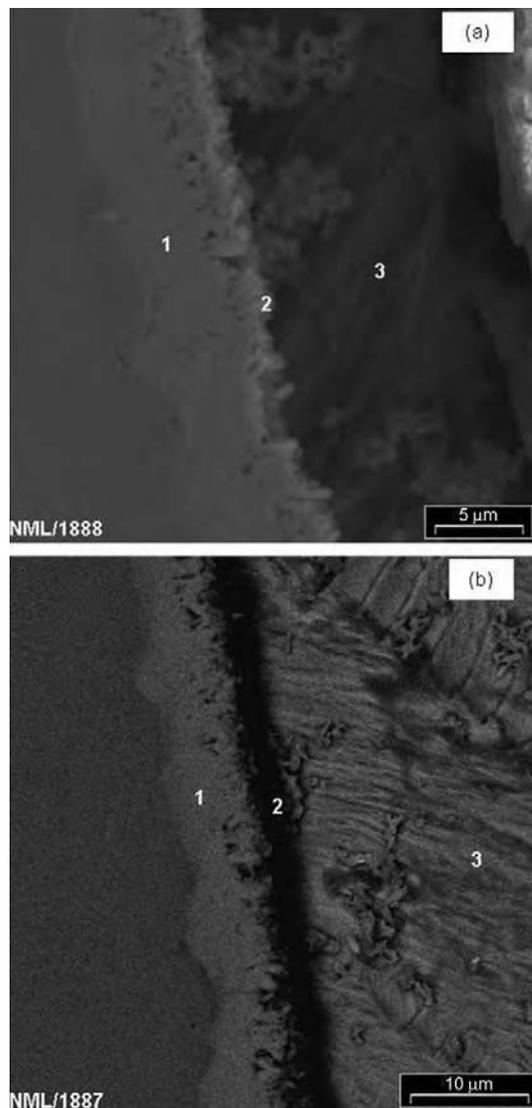


Fig. 1—Scanning electron microphotograph of (a) normal and (b) lumpy wire coating (Point 1 stands for interface layer of coating, 2 for next to interface and 3 for top layer)

Table 1—Chemical analysis of LW and NW coatings at three different locations (layers) marked in Figs 1(a) and 1(b)

Coating	At interface (layer 1), wt. %				Next to interface (layer 2), wt. %				Top layer (layer 3), wt. %			
	Si	Fe	P	Zn	Si	Fe	P	Zn	Si	Fe	P	Zn
LW	2.26	4.89	0.30	89.30	1.91	1.29	0.12	96.75	0.57	3.62	0.08	95.73
NW	0.60	7.43	0.00	91.20	0.11	3.59	0.00	96.14	0.08	1.64	0.00	98.28

of this coating is also observed abnormally high in comparison to NW coating, where no trace of it is recorded. The presence of this element in LW coating may be linked to its higher content in the substrate steel (0.1wt%, Table 2). It may be noted that both Si and P in steels have activating effects on their reactivity with molten zinc¹¹. Their conjoint effect is known as equivalent silicon (Si_{eq}) and is defined as:

$$Si_{eq} = \%Si + 2.5x\%P$$

Table 2 shows that Si_{eq} for LW steel is $0.41 + 0.25 = 0.66\%$ which is well in hyper Sandelin Zone¹². These observations clearly suggest that localized abnormal chemistry of the steel is primarily responsible for lumpy zinc deposition on steel. Presence of normal phases of inter metallic in the NW coating further supports this view. In case of NW coating, the iron content at the interface is 7.43%, which corresponds to delta phase (δ) of zinc-iron phase diagram¹³. This layer is formed during galvanizing of normal steels and controls further reactivity of substrate with molten zinc. The comparison of microstructure of the two types of coatings also supports the above view [Figs 1(a) and 1(b)].

As stated above, the microstructure of the LW zinc coating exhibits different morphologies than the coating on NW. In order to throw more light on this behavior, the morphologies of LW coatings have been studied at higher magnifications to reveal the different phases in the coating (Fig. 2). Presence of scattered blackish structures is noted at its different locations. These phases were analyzed by EDXA and shown by wt% Si (15%), O (5.2%), P (0.2%), Cl (1.41%), Mn (0.4%), Fe (6.60%) and Zn (61%). A stoichiometric calculation for this chemistry indicates the presence of molecule of Zn_2SiO_4 . Theoretically, the content of elements in this compound should be Zn 60%, Si 11% and O 26.5%. While the contents of Zn and Si are comparable, there is much difference in oxygen content. In order to confirm it further, Raman

Table 2—Element concentration in substrate steels of lumpy and normal wire

Elements	Concentration, %	
	Lumpy wire	Normal wire
C	0.80	0.80
Si	0.41	0.14
P	0.10	0.01
Mn	0.80	0.63
Fe	Balance	Balance

spectroscopy of the black phases present in the LW coating was performed by focusing laser beam of the instrument at these phases. The spectra are shown in Fig. 3. It is to be noted here that pure Si exhibits very strong peak at 520 cm^{-1} which is no where present in the spectra. This indicates that Si present on the surface of steel reacts with zinc to form other compounds. Very strong peaks between 2859 cm^{-1} and 2972 cm^{-1} are noted for the blackish Iceland structures. Although there is no reported Raman peak for zinc silicate (Zn_2SiO_4) in literature, the presence of strong peak at 2889 cm^{-1} , which is very closer to the reported peak of SiO_2 (2895 cm^{-1})¹⁴, suggests the formation of silicon based zinc compounds. Similarly, the observed minor peaks at 1063 cm^{-1} and 707 cm^{-1} are closer to peaks of SiO_2 (1060 cm^{-1}) and $FeSiF_6$ (711 cm^{-1})¹⁴. In addition to this the peaks at 1588 and 1347 cm^{-1} are also recorded which are very close to

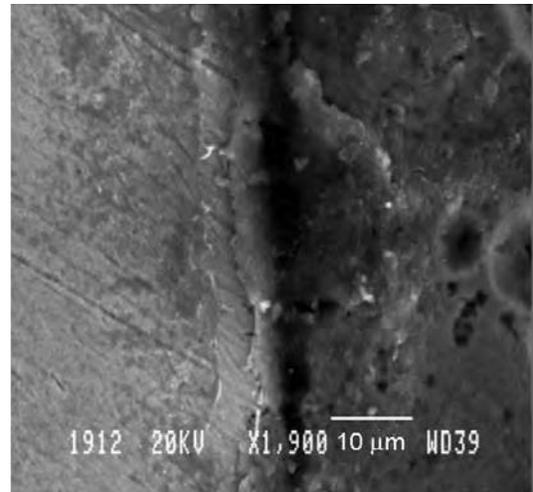


Fig. 2—Scanning electron microphotograph of lumpy wire coating showing black spots

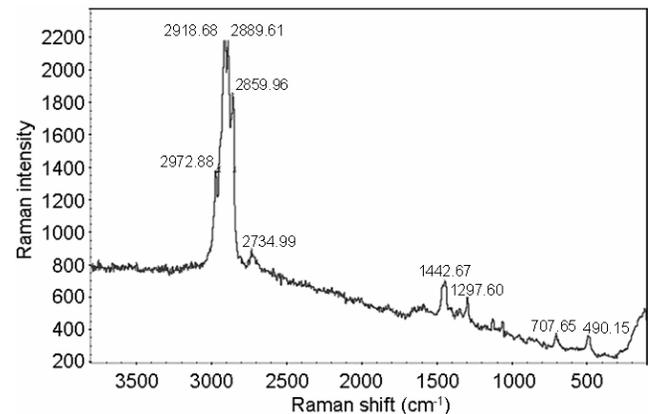


Fig. 3—Raman spectra of lumpy wire coating

the peaks of amorphous carbon¹⁵. The presence of carbon in coating is not surprising in view of the high content of this element in the substrate steel (Table 2).

As stated above, Si content on surface of substrate steel for both types of coatings is considerable. Si content for NW and LW is 0.14% and 0.41% respectively (Table 2), but the blackish scattered structures are noted only in case of LW coating with higher Si content. In order to know more about Si present at the interface coating, laser beam of Raman spectroscopy was focused at the interface of this coating. The observed spectrum is shown in Fig. 4, where two peaks at 967 and 780 cm^{-1} are recorded. These two peaks correspond to silicon carbide¹⁶. However, in case of LW coating no peaks nearer to these are recorded. These facts suggest that low content of Si present on the surface of NW steel reacts with carbon of steel to form SiC, whereas in case of LW interface which contains higher content of Si, it preferentially reacts with molten zinc to form Zn_2SiO_4 , as discussed above.

For normal galvanizing, effective silicon in steels is maintained below 0.09% to avoid their hyper activity with molten zinc¹¹. In special applications, for example in drawing of high strength wire for making ropes for use in hanging bridges, an intentional alloying of steels with solid solution strengthening elements such as silicon, manganese and phosphorus are practiced¹⁷. Although the main purpose of the addition of silicon in steels is to remove oxygen in continuous casting, but in some cases it is also reported to improve strength and fatigue resistance. Unfortunately, the presence of silicon and phosphorus above a critical concentration in steels has adverse effects on galvanized coatings. It is, therefore, recommended to maintain the equivalent silicon in steel (Si_{eq}), which is sum of total % of silicon +

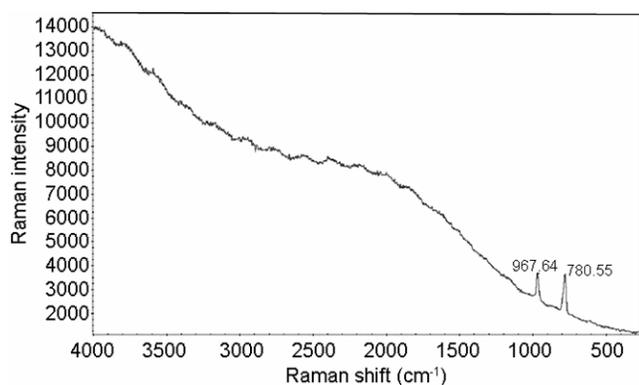


Fig. 4—Raman spectra of normal wire coating

2.5 times of phosphorus; in the range of 0.14 - 0.2% or less than 0.09%. Beyond these limits, a catalytic reaction between steel and molten zinc sets in and the phenomenon is known as Sandelin effect. This hyper activity makes the galvanized coating very thick, porous and brittle. It occurs due to surface segregation of these elements and is governed by a complex combination of several diffusion mechanisms namely bulk, grain boundary and surface. Since diffusivity of phosphorus in steel is comparable with silicon, it also segregates at the surface of steels with silicon. It is reported that during the process of lead patenting of wire, to bring the steel in austenitic phase and hence to have increased strength, silicon from the core of wire diffuses to the surface and forms iron-silicon compounds (Fe_2SiO_4). This compound is insoluble in acid solutions during pickling of steels and remains present as small crystallites on the steel surface. When steel having these crystallites at the surface, enter into molten zinc, it reacts preferentially with zinc in different way than the normal steel. In reaction of normal steel with molten zinc, formation of a compact δ and ξ layers at the interface ensures a uniform reactivity of zinc with the steel surface. However, in case of hyperactive steels, silicon is sparingly soluble in ξ phase (FeZn_{13}) of the coating and segregates at the grain boundaries. Thus, liquid zinc pockets form between the ξ crystallites. This makes the ξ layer of the coating incoherent and porous. A direct reaction between liquid zinc and substrate / δ phase takes place, resulting in excessive loss of iron and formation of ξ crystallites in the liquid. Che *et al.*¹⁸ have shown that excessive silicon accumulates on the surface of the steel substrate due to the low solubility of silicon in the ξ layer after the Fe layer is depleted by the increasing growth of the compound layers. With the movement of $\alpha\text{-Fe}/\xi$ interface towards the substrate by the Fe/Zn reaction, silicon-rich $\alpha\text{-Fe}$ peels off from the substrate and breaks into particles. The particles, much like an inert marker in a Kirkendall effect experiment, move towards the δ layer through the ξ layer because silicon-rich $\alpha\text{-Fe}$ cannot be adsorbed in the ξ layer. On reaching the δ / ξ interface, the particles are quickly dissolved in the δ layer and accelerate its growth, resulting in the gradual disappearance of the ξ layer. At the same time, the normal coating is quickly changed into coatings typical of reactive steels as silicon dissolved in the δ layer soon diffuses toward the ζ layer. A similar process may

occur in the initial stage of galvanizing reactive steels on a small scale, although it is hard to be observed.

Foxt *et al.*¹⁷ have shown that a layer of liquid zinc, saturated with silicon on the steel surface, leads to formation of loose and thick coating during the process of galvanizing¹⁸. The absence of gamma [Γ] layer during the galvanizing of hyper silicon steels is also suggested to be one of the reasons for abnormal coating thickness. Γ Phase in zinc–iron phase diagram corresponds to iron zinc compound with molecular formula $\text{Fe}_3\text{Zn}_{10}$ and forms at interface of steel– zinc coating. Under normal conditions, iron content in the Γ phase ranges from 20.3% to 27.0%. The analysis of LW coating at the interface, however, shows iron in the range of 5% which corresponds to the zeta phase. A thick coating with major ξ phase has poor adherence with the substrate steel and is more prone to shaving during the drawing operations. This observation is in corroboration with earlier reported fact that a higher content of silicon at the interface results in disintegration of Γ phase¹⁸.

The above problem can be solved by minimizing the silicon and phosphorus contents in the steel. However, alloying of steels with higher content of these elements is inevitable for making steel wire ropes with high strength and fatigue resistance. Therefore, suggestion related to control of these elements below Sandelin zone is an impractical solution. Certain steps taken during the process of galvanizing may help to minimize this problem.

If wires after lead annealing and normal pickling are passed through an oxidizing acidic bath such as a mixture of sulphuric and nitric acids, it will dissolve surface segregated Si and P compounds and control lumpy deposition of zinc coating. Another method is to use zinc –nickel alloy in zinc bath that may help to reduce Sandelin effect¹¹. However, this method is reported to have enhanced effects on dross and ash formations. Another practical solution is to flux wire before galvanizing in fluxes based on nickel salts and effective reductants.

Conclusion

The results of this study have confirmed that shaving problem encountered during cold reduction of galvanized wire is caused due to catalytic effects of

surface segregated Si_{eq} on reactivity of steel with molten zinc resulting in lumpy deposition of coating. EDXA and Raman spectroscopy reveal that the possible zinc–silicon phase formed during galvanizing of steel with high Si_{eq} is Zn_2SiO_4 . Very thick layer of zeta phase is formed during galvanizing of this steel. A zinc coating rich in zeta phase is very hard and brittle and results in shaving during cold drawing of galvanized wire.

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