

## METALLIC CORROSION AND ITS CONTROL USING SURFACE MODIFICATION TECHNIQUES

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Metallic corrosion is a very common, but serious problem, which is causing considerable revenue loss throughout the whole world. Mitigation of corrosion requires the application of various engineering techniques and scientific knowledge on the role of the alloying elements in the reduction of corrosion losses and application of the film forming inhibitors are well known. Probe inside the electrochemical nature of the metallic substrates has also resulted in the understanding of the mechanism of passivity. However, in the regime of engineering techniques mention may be made for processes like electroplating, spraying, galvanising and anodising along with those of anodic and cathodic protection methods. These techniques, processes and methods are widely used by the corrosion engineers for reducing the corrosion losses of metallic surfaces. Nevertheless, use of surface modification techniques for the improvement of surface performance appears to be the most promising technique for corrosion control. This technique provides a stronger and more reliable surface alloy layer to be formed on the surface, having a lower level of porosities and higher level of corrosion resistance. This paper has discussed all these aspects, with particular reference to surface modification. Some experimental results have been correlated showing the interrelation of the type of surface modification with the indicator properties like  $I_{corr}$ ,  $E_{corr}$ , mass loss, oxidation rating etc.

**Keywords:** Corrosion, surface modification, corrosion control.

### INTRODUCTION

Metallic corrosion has been responsible for the loss of millions of rupees all over the globe due to the premature disintegration of the metallic surfaces and equipments both in ambient and corrosion environment. A part of this massive expenditure may be saved, if not the whole of it, by the application of suitable quality control measures and the alteration of composition and texture of the equipments and structures, provided appropriate corrosion control methods are employed in such approach. It is known that the reduction of impurities on the substrate (structures and equipments) and simplification of design by the reduction of stiff corners and flattening of the other stress concentration points and profiles reduce the surface corrosion loss to a considerable extent. As such, the application of barrier layers at the metal electrolyte interface and understanding of the correlation of

the surface leaching, nature of the surface and the electrolyte, have travelled a long way. In the initial period of development of the science of materials, scientist had started the stabilisation of natural corrosion product film and also started improving upon the passivity of conventional metallic substrates using inhibitors which either form a film (anodic process) or interfere with the cathodic process. A lot of efforts are also being spent on the composition of the metallic surfaces and also the texture and the microstructure for the reduction of surface leaching rates. Alloying elements like Cr, Ni, Mo etc., have been tried to improve the overpotential of the metallic surface. Heat treatments, particularly stress relieving processes have been designed to reduce the stress concentration on the different points on the surface for an overall reduction of surface leaching rates. Alloying elements are chosen such that they differ very little in the electrochemical potential values resulting in the lower galvanic interaction on the matrix. Engineering techniques

**TABLE.I: Properties of mild steel and slurry metallised M.S.Surface, using chromium powder**

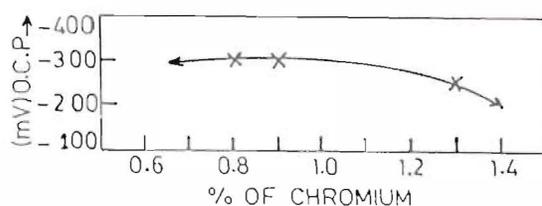
Sample	Microhardness		Potential in mV, w.r.t. SCE (3% NaCl)
	(V.P.N) [case and core]	Thickness (µm)	
Uncoated M.S	250-280	0	-550
Single metallided	333-303	20	-350
Double metallided	365-340	75	-300
Triple metallided	380-360	100	-250

like anodic and cathodic protection are also extensively employed to minimise the losses incurred by the corroding metallic substrates. Nevertheless, the distress of the corrosion in metallic surfaces could not be reduced. This does not mean that corrosion is an insurmountable barrier, although it is practically not possible to stop corrosion completely, whether wet or dry as it is against the basic thermodynamic law, where oxides have lower free energy and form from the environmental interactions of metallic materials. Metals and alloys are only retrieved from the reduction of ores which are basically present in oxide forms.

This paper has discussed all these things with particular reference to the existing conventional corrosion control techniques, using some experimental test results. Some advantages and disadvantages of such processes in the context of dry and wet surface modification routes have also been highlighted in this article.

**EXPERIMENTAL**

Slurry and paste metalliding, using chromium powder have been conducted as per solid state chromiding basics with due weightages for particular temperature of chromiding, exposure in chromiding enviroment, concentration of chromium powder etc.Ethyl silicate is used in slurry treatment for saturating the M.S substrate with Cr,leaving



*Fig. 1: Slurry chromiding*

**TABLE.II: Properties of mild steel and paste metallised M.S.Surface, using chromium powder**

Sample	Microhardness		Potential in mV, w.r.t. SCE (3% NaCl)
	(V.P.N) [surface]	Thickness (µm)	
Uncoated M.S	250	0	-400
Single metallided	300	25	-200
Double metallided	325	40	-50
Triple metallided	350	40	-50

the SiO<sub>2</sub> along with the Al<sub>2</sub>O<sub>3</sub> inert cover in the coating structure.

In paste chromiding ,reactive compounds of the class of ammonium flouride are employed,where flouride ion helps in surface etching and also generating reactive intermediates,which helps in the generation of Fe-Cr interaction products.Diffusion of Cr in the substrate is only marginal in the slurry process.While it is not so in the paste process.Watt's Nickel and electrolytic Nickel are obtained on M.S substrate as per ASTM specifications.Ni-P-B barriers are obtained on M.S subtrate using current assisted electroless routes. Nickel salts, phosphoric acid, sodium hypo-phosphate, sodium borohydrate, ethyl silicate, Al<sub>2</sub>O<sub>3</sub>, NaCl etc used in this study are of A.R. quality.Chromium powder used is of fine variety (15µm) containing 99.9% Cr.

**DISCUSSION**

Experimental test data has been depicted through three tables (Tables I,II,III) and four figures (Fig 1,2,3,4).It is clear from these tables and figures that diffusional alloy layer

**TABLE.III: Effect of heat treatment on the corrosion resistant properties of C.R.N.O (Transformer) Steel after coating with crystalline or amorphous Ni**

Coating on M.S	Thickness (µm)	Corrosion Rate (g/cm <sup>2</sup> x 10 <sup>-3</sup> )		Temp and time of heat treatment
		Before	After	
Watt's Ni	30	0.22	6.11	673 K/1hr
Electroless Ni	5	0.22	0.05	473 K/2hr
Ni-P-B coating (Amorphous)	10	0.03	0.05	473 K/2hr

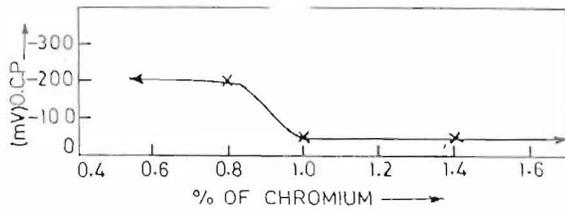


Fig. 2: Paste chromiding

formation, has an edge over the other processes of metallic coatings etc, due to the superior adherence of the diffusion coating to the metallic substrates. Heating at elevated temperatures also favours the formation of some thermally activated reaction products and interaction compounds, allowing coating dilution and superior adherence.

Table I reveals the properties of M.S surface and that of the slurry metallized one on M.S surface, using Cr powder. It is very clear that increase in the no. of the chromiding steps have resulted in the progressive increase of the barrier layer hardness and also that of the coating thickness of Cr.

Table II reveals the corresponding values as in Table I for the paste chromided panels. It is seen that hardness values are more or less identical although, the values of coating thickness with dilution at the interface is somewhat less. However, the surface potential values are comparatively more positive than those of the slurry chromided one. The surface potential values are positive and they are in the following range. Triple metallized > double chromide > single chromide. Higher coating thickness in the former case is due to the lower substrate dilution such that Cr remains in the metallic form of coating, while in the fluoride activation plus chromiding process, most of chromium is diluted within a specific zone of the surface of the substrate such that accumulation of the metalliser on the surface is almost nil. Highly positive potential value of the paste chromided panels may be attributed to such diffusional alloy layer formation and dilution of metallic dopant within the substrates. The hardness values in both these cases correspond to the Ferrite-Pearlitic matrix with solid solutioning effect of Cr in Ferrite and that of pure Cr.

Table III reveals the effect of heating on the MS substrates coated with Watt's Ni, electroless Ni and also current assisted electroless Ni-P-B. It is seen that Watt's Ni is considerably destabilised by heating at 673 K, which is much below the diffusional requirements of Ni within the Ferrite-Pearlitic matrix (MS material) resulting in higher corrosion

rate values. It is attributed to the oxidation of the MS substrate, through the porosities in the Ni deposit, while in the case of electroless (Ni-P) and current assisted electroless (Ni-P-B). Such things are ruled out as the level of porosities are much less in such barriers, particularly for 473 K heating. It appears that there is further sealing of porosities, as a result of formation of metal phosphides. Such thermally activated movements might have resulted in dilution of interfacial cases resulting in better adherence and lower galvanic stresses at the interface. Above 673 K, the micro-crystalline Ni-P, Ni-P-B surface may be changed to a macro crystalline one and at that elevated temperature, the possibilities of boride (Ni<sub>3</sub>B) formation at the interface cannot also be ruled out. Fig. 1 reveals correlation of surface potential (OCP in mV) and % Cr. It is seen that the potential tends to a more positive direction, with increase in Cr % and the number of metallizing steps. More or less similar trend is observed in Fig. 2 to the case of paste chromided steps. However transition to a more positive direction only takes place beyond 1% Cr in both slurry chromided and paste chromided steps. Fig. 3 reveals the relative advantages of surface modifications in terms of corrosion resistance, adhesion and porosities. It is seen that, compared to the paint coating and electroplating, surface modification provides superior corrosion resistance and adhesion coupled with lower porosity level. Fig. 4 reveals the disadvantages of surface modifications over that of the paint coating and electroplating. It is observed that surface modification had a higher risk of thermally induced effects of oxidation during air diffusion along with rupturing, cracking and warping. However, use of inert environment and control in furnace design (temperature along the working length) and judicious selection of the temperature and exposure period of diffusion may reduce these hazards to considerable extent.

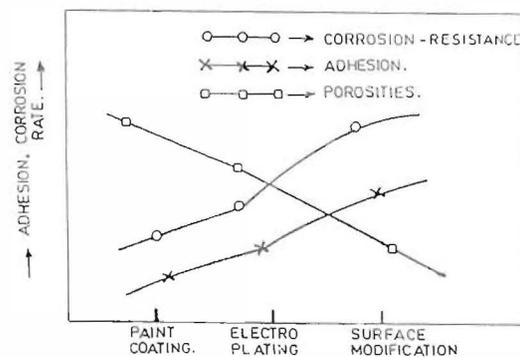


Fig. 3: Advantages of surface modification

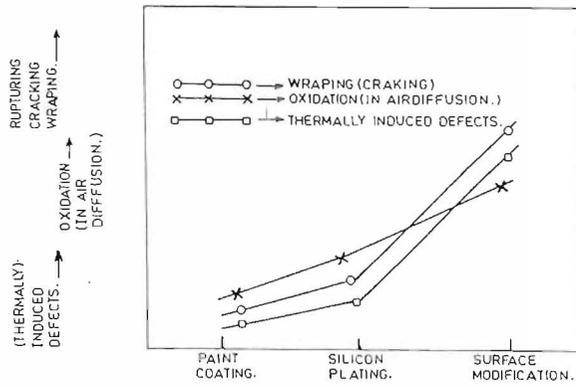


Fig. 4: Disadvantages of surface modifications

### CONCLUSION

It appears from these correlation of data in both the tabular and graphical form and discussion on the conventional process of surface protection that surface modification processes are innovative, as far as corrosion resistance and reliability of coatings are concerned. It further appears that the resistance may be improved in a progressive manner by increasing the concentration of the metallizing agent, as for

example Chromium in case of chromiding. This trick can easily be accomplished by increasing the number of metallizing steps of the process. Compared to the conventional painting (polymer coating) and electroplating, surface modification processes appear to have an edge in terms of corrosion resistance, coating adherence and porosity levels. Moreover, such processes do not require substantial maintenance cost, like passage of current in cathodic protection and anodic protection, intermediate cleaning and repainting in the case of polymer coating. A properly modified surface may work years together without any subsequent attention.

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### REFERENCES

1. Unique model of surface modification by D Mukherjee, *Tool and alloy steels*, Vol 29 No.12 December (1995) 419
2. Viable metallurgical treatments and diffusional coatings for improving the performance of reinforced bars D Mukherjee, *Tool and alloy steels*, Vol 30 No.1 January (1996) 17