JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 8 submitted 5 February 2014

Hardness and corrosion resistance characteristics of trivalent chromium electrodeposition – An eco friendly process

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Abstract

An attempt has been made to develop an eco friendly trivalent chromium process as an alternate to hexavalent chrome plating for industrial steel components. Vicker's hardness and A.C impedance studies revealed that the coatings exhibit high hardness and good corrosion than mild steel in sea water medium. XRD and SEM results confirmed precipitation of chromium on iron matrix which improved the mechanical properties on the heat treated mild steel surface coated by trivalent chromium.

Keywords: trivalent chromium, eco friendly, impedance, corrosion

Introduction

The studies on industrial coatings based on electrodeposition of trivalent chrome coatings in recent years is gaining much importance as they find a great variety of applications in different fields like automotive and gas turbine with less toxicity.

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Hence the present investigation is on these aspects. D.E. Crotty [1] and C. Barnes [2] have reported a Chromium chloride (source for metal ions) ,Boric acid (Buffer to maintain acidity of bath) , Ammonium thiocyante (Complexing agent), 2-chlorophenyl glycine (mild buffer) and ammonium chloride (stabilizers) based electroplating trivalent chromium bath. But bath stability was reported to be confined to the pH (bath acidity) range 2 - 2.2. In the present investigation, it is aimed to develop a new Cr^{3+} based bath to obtain a corrosion resistant coating as a replacement deposition for hexavalent chrome plating.

Experimental

Materials

Chromium Trichloride ($CrCl_3$) - 41 g/l

Boric acid - 72 g/l

2-Chlorophenyl glycine - 18.5 g/l

Ammonium thiocyanate - 30g/l

Ammoium chloride - 35g/l

Current density - 65 mA/cm^2

pH - 2- 2.2

plating time - 2- 90 minutes

Deposit thickness - (0.4 microns - 32 microns)

In the case of electrodeposition of trivalent chrome coatings, the bath stability is vulnerable and it is sensitive to the presence of impurities or any foreign particles. Also the rate of deposition is very low. Hence the use of suitable complexing agent is imperative. The complexing agent used in the study was ammonium thiocyante (NH_4CNS). This forms a high stable complex with Chromium as Cr(III)-CNS.NH_4 . The judicious formulation of the corrosion resistant coating bath was one of the targets of the present investigation.

The selection of the buffering agents (Boric acid and 2-chlorophenyl glycine) were based the colour of the resultant coatings. These buffering agents do not give off fumes during electroplating of trivalent chromium. These are high efficiency and offer good coverage of chromium coatings on the steel surface. Hence their addition in the nickel bath could be expected to yield coatings of superior mechanical properties.

Methods

The kinetics of the deposition was followed through the conventional weight gain method [4-6]. A.C impedance was carried out to understand corrosion resistance of electro coatings. XRD studies were performed for the deposits to understand the phase transformation and the extent of crystalinity of the phases. The microhardness of the coatings was analyzed by Vicker's micro hardness tester at a load 100g. An indentation was made by diamond pyramid of the hardness tester, from the diagonal of the diamond indentation, micto hardness was read directly. The experiments were repeated for 3-4 times at various parts of coated steel and uncoated steel. Then the average of the microhardness values was taken. The SEM studies have been made to understand the surface morphology of the trivalent chrome coatings.

Evaluation of the deposits for their special properties

The microhardness and corrosion resistance properties of the coatings were evaluated through Vicker's micro hardness tester and A.C impedance techniques. A justification of the properties of the deposits has been explored through XRD and SEM studies.

Results and Discussion

Weight gain studies

The results of black coatings obtained in the present study by weight gain method are presented in table 1.

Rate of deposition = Weight gain (in g) x 10^{-4}/ Density of (Cr} x Area x time (in min.)

The rate of deposition at various current densities was studied. It can be seen from the table 1 that the present trivalent chromium plating formulation can be used for decorative applications (thickness of coatings should be less than 1 micron) and engineering applications (above 30 microns).

Hardness measurements

The hardness of the electrodeposited trivalent chrome coatings measured by Vicker's hardness tester is given in Table 2.

The higher hardness of trivalent chrome coatings can be ascribed to the formation of uniform metallic layers in the coatings[7-9].

Corrosion resistance by A.C. impedance analysis

The Nyquist plot for uncoated steel and trivalent chromium coated steel in 3.5% NaCl was shown in figure 1. The larger semi circle was produced by trivalent chrome coatings whereas smaller semicircle was obtained for uncoated metal. It can be easily observed from the figure that R_t values are high in composite coating than uncoated steel. This indicates that trivalent chrome coating was more corrosion resistant than mild steel. Thus the chromium incorporation in the steel surface produced higher resistance to corrosion. Similar observation has been made earlier by Karthikeyan et.al[10].

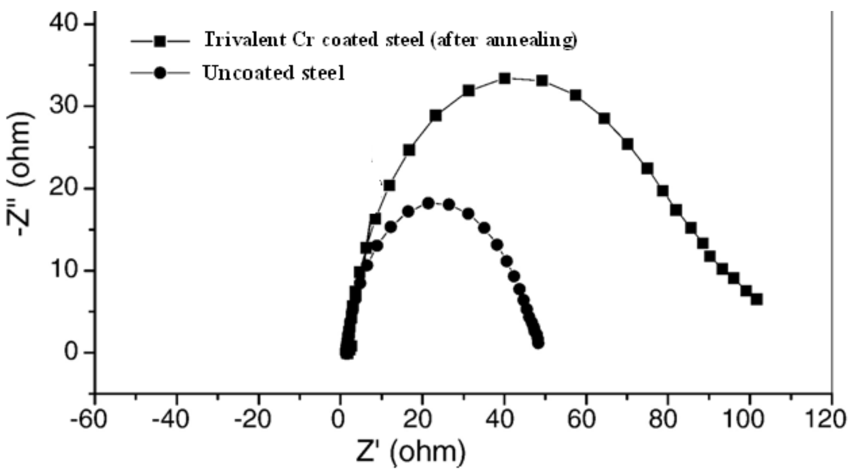

Figure . Nyquist plot for corrosion resistance trivalent Cr on steel

Surface morphology of the trivalent chrome coatings

Scanning Electron Microscopic studies (SEM)

Figure 2 indicates the SEM photos of uncoated steel exposed in sea water medium (3.5%NaCl). The formation of pits and roughness were clearly appeared due to the attack of chloride ions on steel surface. The appearance of uniform layer along with globular regions with quasi-circular domain boarders of trivalent chrome coatings was visibly seen in figure 3 and after annealing the coatings (figure 4) became more

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compact with minute micro line cracks indicates the reduction of distance between each trivalent chrome coatings in their corresponding lattice planes such as (110) and (211). These results were in good agreement with XRD values.

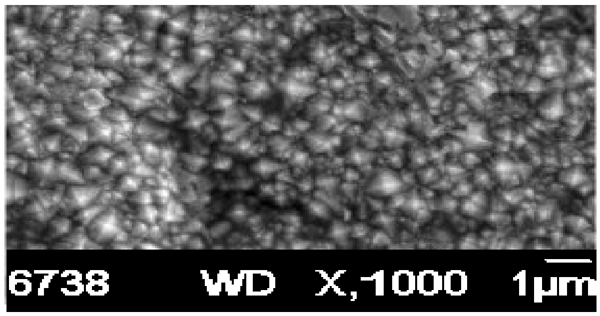

Figure 2. SEM image of uncoated mild steel exposed in sea water medium

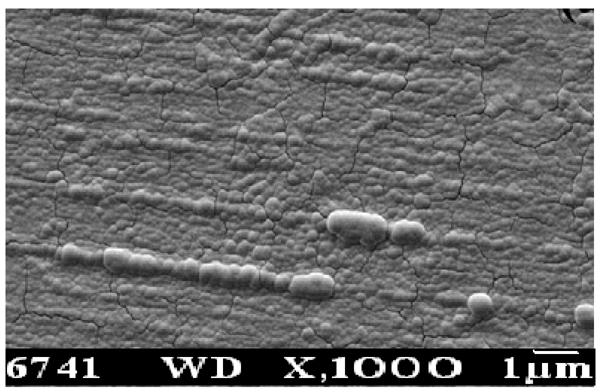

Figure 3. SEM image of trivalent chromium coated mild steel exposed in sea water medium

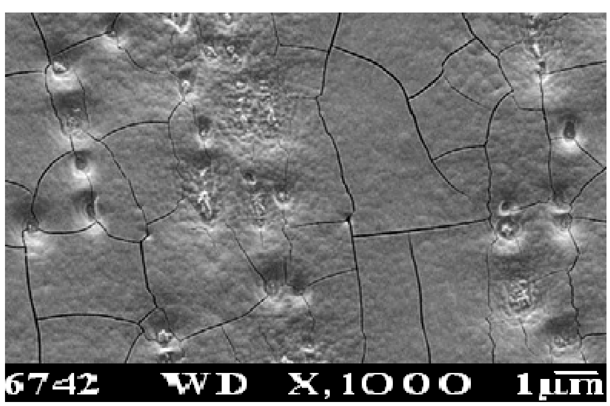

Figure 4. SEM image of trivalent chromium coated mild steel (annealed at 200⁰C) exposed in sea water medium

XRD analysis

Figure 5 shows XRD patterns of deposited coating by trivalent chrome electroplating. In order to analyze the structures of deposited coatings (after annealing at 200ºC) with crystalline structure, their X-ray diffraction patterns were compared with the ASTM data[11-12]. In the case of deposited coatings, two amorphous peaks at 42.8, 49.6 and 73.2 were obtained for chromium deposits. It was found that the trivalent chromium deposits have a peak at (110) and (211) planes[13].

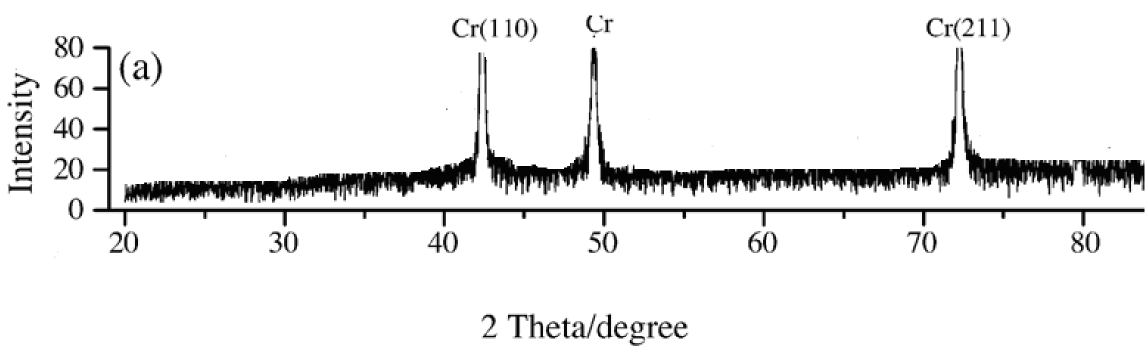

Figure 5. XRD for trivalent chrome coated steel (heat treated at 200ºC)

Conclusion

1. The developed trivalent chrome coatings is absolutely free from pollution to environment.
2. The coatings exhibited high hardness and corrosion resistance both in the as plated and heat treated conditions.
3. SEM and XRD studies proved that the trivalent chromium coatings improved the mechanical properties.

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Table 1: The results of weight gain studies obtained for black coatings:

S.No	Trivalent chrome coatings	Thickness	Nature of deposit
1.	Mild steel coupon,A (50 mA/cm^2, 2 min)	0. 25microns	white
2.	Mild steel coupon,B (65 mA/cm^2 , 2 min)	1.5 microns	White with uniformity
3.	Mild steel coupon,C (75 mA/cm^2 , 8 min)	1.2 microns	Semi white with uniformity.
4.	Mild steel coupon,b (65 mA/cm^2 , 90 min)	32 microns	White with uniformity

Table 2 Vickers hardness values for black coatings:

Substrate	Hardness in V.H.N (load 100g)
Mild steel	185
Trivalent chrome coatings (32 microns)	485