

Characterization of Chromium Electrodeposits Obtained From Trivalent Electrolytes Containing Formaldehyde as Additive

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Abstract: Herein we examine the effect of formaldehyde on chromium electrodeposits obtained from trivalent chromium electrolytes containing urea and formic acid as complexing agents. Indigenous experimental set up was made using platinized titanium as anode and mild steel as cathode. The ensuing physico-chemical properties of the deposits were characterized and analyzed by different characterization techniques such as XRD, SEM, EDAX and FT-IR. Corrosion measurements such as Tafel polarization and AC impedance spectroscopy were carried out in 0.2M H₂SO₄. These studies revealed that chromium electrodeposits obtained from the electrolyte containing 100 ppm of formaldehyde, showed the good corrosion resistance property towards acidic solution. The electrocrystallization of chromium during electrodeposition favored by the presence of formaldehyde resulted in chromium deposits of nano scale. i.e. 23 nm. EDAX analysis revealed the elemental composition of obtained electrodeposits. The bond formation between formaldehyde and chromium metal was established by FT-IR studies.

Keywords: Electrodeposition. Trivalent chromium. Formaldehyde. Corrosion.

complexing agents, like urea, formic acid, glycine, DMF etc... [4,5].

1 Introduction

Mild steel has been widely used in many chemical industries due to its low cost and easy availability for fabrication of reaction vessels, tanks and pipes, etc. Mild steel also finds some mechanical, structural application in industries [1]. Chromium metal based on its usage it is named as decorative and hard chromium. Its high hardness, superior wear and high corrosion resistance lead to the usage of this as surface coating for lanterns, hand tools, automobiles, aero-space parts, devices used for cutting etc... Globally its usage as decorative chromium was about 16 billion US dollars in 2003, while its usage as hard chromium was about 3.2 billion US dollars [2]. Conventionally chromium is electrodeposited from highly toxic hexavalent chromium bath. In European Union, China, Japan and in many other countries its usage has been restricted and it is highly hazardous when exposed to the skin [3]. Among many alternatives, trivalent chromium based electrolyte is considered as the prospective aspirant to replace the perilous hexavalent chromium without changing its properties. Number of papers are published, affirming that chromium coatings can be obtained from trivalent chromium baths, with the addition of organic

Several researchers showed their interest in depositing chromium from urea and formic acid baths, [6-8] because of its high quality thick chromium-coatings and higher current efficiency. Organic additives have been commonly used in the formulation of electroplating bath chemistries [9]. Their usage has been increased tremendously due to its synergetic effect on electrodeposits. Additives in electrolyte acts as stress relievers and brightening agents [10-11]. Enhances the rate of nucleation process resulting in high strength and hardness [Hall Petch relation]. Improves corrosion and wear resistance [12-13] and suppress the hydrogen evolution during electrodeposition [14]. Inspired by these works and others, a thorough experimental study on the effect of formaldehyde on chromium-coatings obtained from chromium-bath containing urea and formic acid as complexing agents.

2 Experimental

2.1 Electrodeposition aspects

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All the chemicals used were of AR grade and the bath was prepared with double distilled water. Bath composition used for electrodeposition of chromium is mentioned in the Table 1. pH was maintained at 1.6. The following pretreatment process is espoused: mild steel specimens were sluced thoroughly with double distilled water, ultrasonicated in acetone for 10 minutes and the rear end was masked with scotch metallic tape. Prior to each deposition, specimens were activated in 10% H₂SO₄ solution, swilled with distilled water and instantly placed in the electrolyte. Chromium coatings were electrodeposited on the mild steel substrate (25 mm x 25 mm x 0.3 mm) by using dc power supply. Platinized-titanium (25 mm x 25 mm x 1.5 mm) was used as anode. The electrooxidation, of Cr (III) to Cr (VI) takes place at low rate, so there is no need of using separator in between cathodic and anodic compartments [15]. All the experimentations were carried out in a usual thermostated glass cell.

Table 1. Basic bath composition and operating conditions

Elements present in the bath	Content (M)	Working conditions
Cr ₂ (SO ₄) ₃ · 6H ₂ O	0.5	Temperature- 32-33°C
HCOOH	0.5	Current density 10 Adm ⁻²
CO(NH ₂) ₂	0.5	pH - 1.6
Al ₂ (SO ₄) ₃ · 18H ₂ O	0.15	Duration- 5 min
Na ₂ SO ₄	0.3	Anode- platinized titanium
H ₃ BO ₃	0.5	Cathode- mild steel
NaC ₁₂ H ₂₅ SO ₄ (SDS)	0.1g/l	
HCHO	0-1000 ppm	

2.2 Characterization techniques

The pH value was measured by using ELICO Li120 pH meter. The X-ray diffraction (XRD) study was carried out using a Shimadzu XRD6000 X-ray diffractometer using CuK α radiation. The crystallite sizes of the coated samples were calculated using Scherrer's formula. Miller indices (hkl) values were taken from standard JCPDS data. An JEOL model JSM-360 SEM-EDAX was used to determine the elemental composition and morphology of the coated specimens. Electrochemical measurement techniques are considered as non-destructive and less time consuming compared with weight loss measurements in laboratory work [16].

Electrochemical measurements were done using a three electrode cell system. Electrodeposited chromium mild steel serves as working electrode, platinum wire as counter electrode, and saturated calomel electrode as reference electrode. The polarization curves and A.C impedance spectra were carried in 0.2 M H₂SO₄ solution with an exposed area of 0.2 cm² at room temperature. After the steady state open circuit potential (OCP), its polarization

curve was recorded at a constant scan rate of 10mV/S. The electrochemical impedance spectroscopy measurements (EIS) were recorded at OCP value in a frequency ranging from 1Hz to 100 KHz with an AC amplitude of 5 mV. All the electrochemical techniques were carried out using a potentiostat of CHI660C instrument. Complex formation was confirmed through Fourier transform infra-red spectrometer (Brucker-Tensor 27) in ATR mode.

3 Results and Discussion

The electro-deposition of chromium metal proceeds in three steps along with hydrogen evolution [17, 18]

Incomplete reduction of Cr⁺³ ions



Electrodeposition of chromium metal



Simultaneous hydrogen evolution



3.1. Polarization Measurements

The polarization curve of deposited chromium coatings, in absence and presence of formaldehyde in the bath solution are shown in Fig. 1. Polarization parameters drawn from Tafel plots such as corrosion potential (E_{corr}), corrosion current (I_{corr}), linear polarization resistance (R_p) and corrosion rate (CR) were reported in Table 2. From Table 2 it is clear that chromium electrodeposits (100 ppm), yielded low I_{corr}, and corrosion rate values. This reveals that chromium deposits obtained at this concentration enriches the corrosion resistance property of mild steel in 0.2M H₂SO₄ medium. E_{corr} value also shifted to more noble direction. Higher R_p value also suggest that metal dissolution process reduced in 0.2M H₂SO₄ medium. However on further addition of formaldehyde above 100 ppm, to the basic bath resulted in gradual increase in the corrosion rate and I_{corr} values.

Table 2. Polarization parameters derived from tafel plots for chromium electrodeposits in 0.2 M H₂SO₄

Concentration of HCHO (ppm)	E _{corr} (mV vs SCE)	I _{corr} (μA/cm ²)	CR (mm/year)	(R _p) (Ω cm ²)
Without aldehyde	-23	24.6	1.03	1720.1
100	-19	6.8	0.28	6364.3
250	-525	72.4	2.97	226.1
500	-578	18.7	7.71	133.7
750	-529	42.9	1.76	398.8
1000	-527	76.5	3.14	303.4

3.2 Electrochemical Impedance measurements

Fig. 2 depicts the Nyquist plots of chromium

electrodeposits obtained in absence and presence of various concentrations of formaldehyde respectively. All the AC impedance measurements were done at their respective OCP values. Charge transfer resistance (R_{ct}) values obtained from the diameter of semicircles are shown in Table 3. R_{ct} value increased on addition of 100 ppm of formaldehyde to the bath solution from 53.76 to 615.94 Ωcm^2 to that of blank. Increase in the R_{ct} value attributes to the formation of protective layer on the deposit surface that reduces the ion diffusion process. The Increase in the R_{ct} value also corresponds to the decrease in corrosion rate (CR) [19]. However upon increasing the concentration of formaldehyde, R_{ct} value decreased stating that film defense functioning worsens if too much of formaldehyde is present in the solution. Obtained impedance results are in good agreement with the Tafel results.

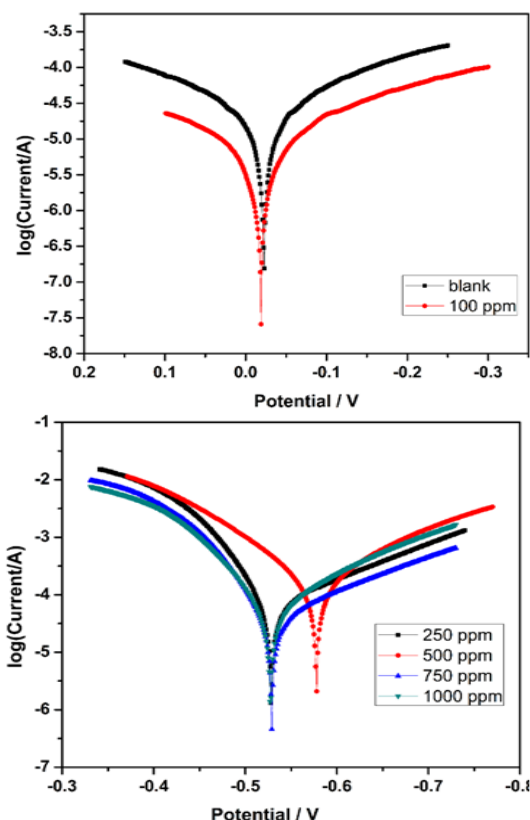


Fig. 1. Typical Tafel plots of chromium coatings in 0.2M H_2SO_4 medium. The electrodeposits obtained in absence and in presence of different concentrations of formaldehyde in bath solution.

Table 3. Impedance values of chromium electrodeposits in 0.2 M H_2SO_4

Concentration of HCHO (ppm)	R_{ct} ($\Omega\text{ cm}^2$)
Blank	53.76
100	615.94
250	20.77

500	23.62
750	30.53
1000	31.00

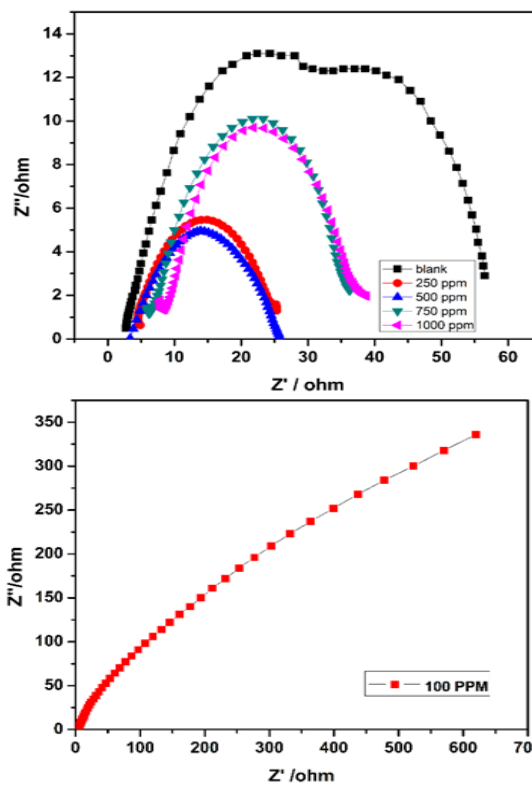


Fig. 2: Nyquist plots of chromium coatings in 0.2M H_2SO_4 medium. The electrodeposits obtained in absence and in presence of different concentrations of formaldehyde in the bath solution.

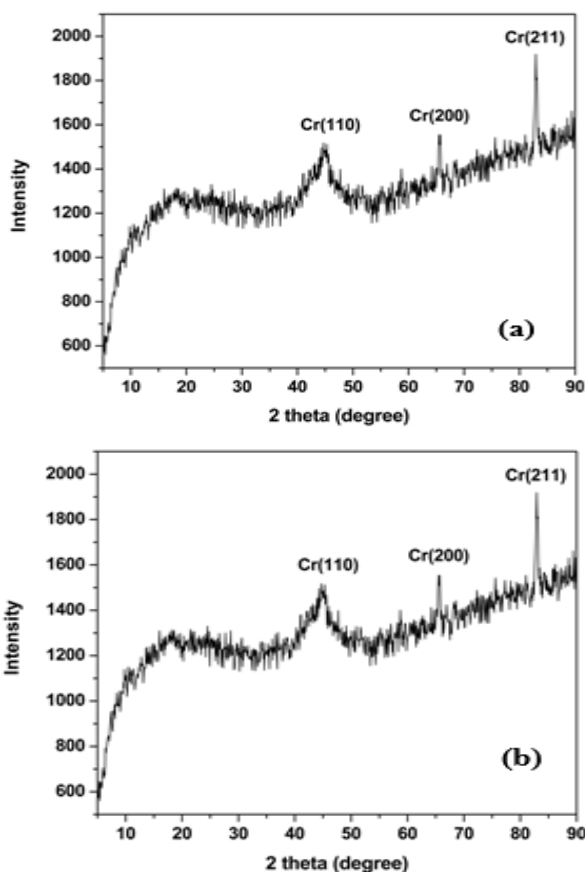
3.3 X ray diffraction studies

The XRD patterns of chromium electrodeposits without and with 100 ppm of formaldehyde are shown in Fig. 3(a-b). Chromium peaks were present at 2θ angles of 45, 64.5, and 84. The main peak corresponds to chromium (110) plane and others at (200) and (211) planes, as reported in the previous literature [20, 21]. The deposited coatings represents the body centered cubic crystalline structure revealed by comparing XRD patterns with JCPDS card no Cr-06-0694. The average crystallite size of Fig.3(a) is 22 nm and Fig.3(b) is 23 nm, calculated using scherrer equation. Therefore from XRD patterns, it is made known that nanocrystalline chromium deposits were obtained without any secondary compounds such as Cr-o (oxides or hydroxides).

3.4 SEM-EDAX

Fig. 4(a-b) depicts the SEM images of chromium electrodeposits without and with 100 ppm of formaldehyde. Both the images represents smooth surface,

with some microcracks that may be due to the reduction of hydrogen ions during electrodeposition process. However on the top, very few spheroids are seen with fewer diameters. The atomic weight percentage of the elements present in the electrodeposits obtained at 10 Adm^{-2} without and with 100 ppm of formaldehyde was shown in Fig. 5 (a-b). The electrodeposits have chromium metal as the major element. In Figure 5(a) we observe the presence of less percentage of iron may be due to porous and micro cracks on chromium-carbon deposit such that the characteristic X ray ($\text{FeK}\langle\alpha\rangle$) could escape through the deposit to



detector. In Fig. 5b we notice the presence of traces of carbon may be due to the chemical interaction of active chromium adatoms with adsorbed organic molecules and is basically a non-Faraday process [22].

Fig. 3. XRD spectra of chromium electrodeposits (a) in absence (b) in presence of formaldehyde (100 ppm) in the bath solution.

3.5. FT-IR spectra

In order to substantiate the complex formation between chromium and formaldehyde, the coated samples, from baths without and with formaldehyde were analyzed with the aid of FT-IR spectroscopy in ATR mode. The Fig. 6a represents the strong absorption bands at 650 and 600 cm^{-1} that confirms the presence of Cr-O bond and traces of SO_4^{2-} ions [23]. In the Fig. 6b we can see the characteristic

absorption peaks at 1646 cm^{-1} that attribute to the presence of C=O group, and further the bands at 2891 , 2815 , 1497 cm^{-1} represents the asymmetric, symmetric, scissoring and wagging vibrations of $-\text{CH}_2$ group respectively, confirming the presence of formaldehyde. The slight shift in the bands from 650 to 605 cm^{-1} clearly indicates that metal has been coordinated with the oxygen atom of carbonyl group of formaldehyde. Based on these annotations, we confirmed the chromium-formaldehyde complex formation on the surface of the metal coating.

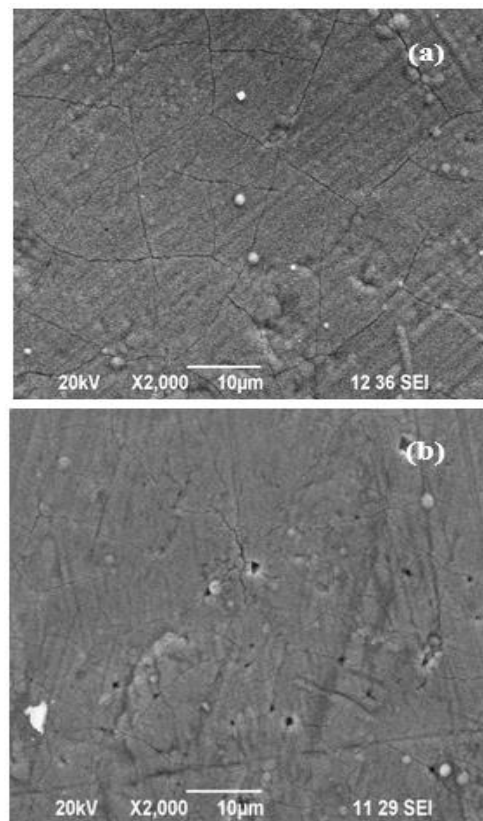


Fig.4. SEM micrographs of chromium electrodeposits (a) in absence (b) in presence of 100 ppm of formaldehyde in the bath solution.

3.6. Mechanism

The formation of critical micelle concentration is viewed as a mechanism of the action of organic compounds on the electrodeposition of metals [24]. The AC impedance and Tafel polarization techniques implies that formaldehyde offers preminent corrosion protection at certain concentration (100 ppm). The corrosion inhibition effect in 0.2 M sulfuric acid by chromium electrodeposits obtained in absence and presence of formaldehyde can be illustrated based on the chemisorption mechanism. This takes place due to the interaction of lone pair of electrons present on the oxygen atom of carbonyl group (C=O), along with growing chromium nuclei during electrodeposition. Here the electrons transferred from oxygen atom occupies the

outer empty orbital's of chromium atom and forms a complex with varying stabilities. From SEM-EDAX (Fig.4.a) data it is made clear that blank electrodeposit is porous with observable microcracks. This results suggests that non-hardened and flimsy chromium deposits obtained on the mild steel such that the chromium dissolution increases in the acidic medium that results in the low charge transfer resistance ($53.6 \Omega\text{cm}^2$).

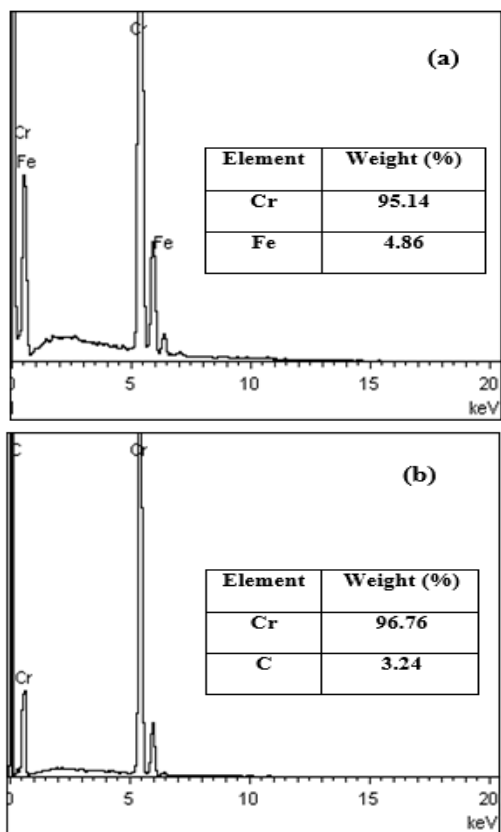


Fig. 5. EDAX spectra of chromium electrodeposits (a) without (b) with 100 ppm of formaldehyde

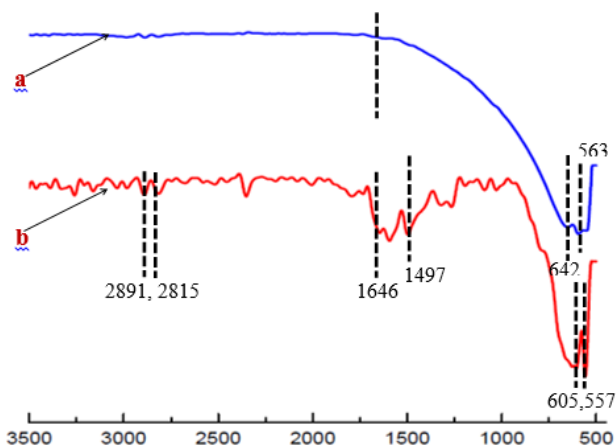


Fig. 6. FTIR spectra of chromium coatings (a) without aldehyde (b) with formaldehyde (100ppm)

Upon addition of formaldehyde (100 ppm) to the bath, these carbonyl groups chelate with chromium ions and move towards into larger pores/fissures thereby forming a thin film on the surface of chromium deposits, notably reducing the porosity of surface film and making the surface film denser. This is how, the seepage of corrosive species becomes arduous and results in the increase of charge transfer resistance ($615.94 \Omega\text{cm}^2$). The increase in the diameter of nyquist plot (Fig. 2) for chromium electrodeposit containing 100 ppm of formaldehyde than that of blank one states that the addition of formaldehyde to the trivalent chromium bath results in the high corrosion resistant chromium electrodeposits. Further on increasing the concentration of formaldehyde, film functioning deteriorates that could be due to large pores and cracks that are accessible to corrosive species. Nevertheless there are still numerous tiny film pores that can be penetrated by corrosive species but not by aldehyde molecule that can act as an active corrosion site [25].

From this, it is clear that upon addition of 100 ppm of formaldehyde to the bath solution resulted in the formation of high dense film on the surface of chromium deposits, which isolates the metal from corrosive medium. The schematic representation of chromium-formaldehyde complex adsorption onto the metal is shown in Fig.7.

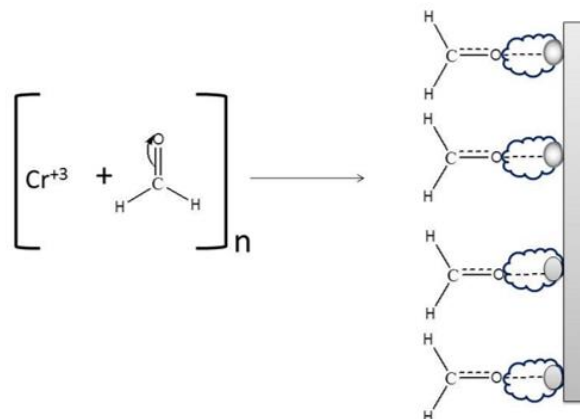


Fig. 7. Schematic representation of aldehyde adsorption onto the alloy surface.

4 Conclusion

In conclusion, we have studied the effect of formaldehyde on chromium electrodeposits derived from trivalent electrolytes. Higher R_{ct} value obtained at 100 ppm concentration (optimum) for chromium electrodeposits infer that ion diffusion process was reduced that aids in reducing the corrosion rate. Corrosion measurements demonstrates that formaldehyde follows adsorption mechanism. XRD calculations reveals that nanocrystalline deposits were obtained on average crystalline size of 23nm. EDAX spectra distinctly established the fact that 96.76 (w/w %) of chromium was obtained on addition of formaldehyde (100 ppm). SEM studies showed the smooth

and uniform surface of chromium deposits specifying the presence of formaldehyde (100ppm) is vital with that of blank one. FT-IR spectra supports for its adsorption mechanism.

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