SPEAKERS
(Basic Corrosion)


National Metallurgical Laboratory, Jamshedpur -7.

CORROSION RESISTANT ELECTRODEPOSITED ZINC COATING FROM ZINC DROSS

ABSTRACT:
Electrodeposition of metals from aqueous solution produces a variety of metal/alloy coatings. Zinc alloy coatings are obtained by electrogalvanising of pure zinc. Properties of electrogalvanised steel like corrosion resistance spot weldability and adhesion are superior to hot-dip galvanised steel. In the present investigation, an attempt has been made to study electrodeposition of zinc from solid zinc dross as an anodic material on steel sheet acting as cathode and an aqueous bath containing different concentration of Cl- ions, ammonium salts and conducting substances at room temperature. An acid chloride bath was mainly used at different pH values. Very thin adherent and impervious coating was obtained on steel sheet. The zinc coating so obtained by electrodeposition was finally passivated to minimize white rust. X-ray diffraction, coating thickness, atmospheric exposure test, electrochemical test, microhardness and cathodic efficiency of zinc coated substrates were carried out. Salt-spray test on the coating was performed for 15 days. Polarization experiments were carried out in 3.5% NaCl solution using EG&G PARC-273A model Potentiostat/ Galvanostat. Open circuit potential (OCP) and corrosion potential (Ecorr) were recorded. The process developed is very simple, economically viable and eco-friendly.

INTRODUCTION:
Electrodeposition of zinc and its alloys has been of great interest because of expanding demand for electrogalvanized and zinc alloy plated sheet steels for automobile and appliance exteriors panels in addition to the increasing application of zinc in electrochemical areas such as generators. The electrodeposition has been studied electrochemically and metallurgically to lead to improve plating process and functions of the electroplated surface. The paper gives an overview of corrosion behaviour and discusses the methods used to produce coating through electrochemical route by chloride based bath and describe the type of metal coating and its physical and chemical properties as well as their corrosion characteristics.
In the present investigation, an attempt has been made to study the electrodepositions of value-added zinc coating from zinc dross on steel sheet or tube acting as cathode with different concentrations of ions. The cell temperature was varied between 20-30°C with constant stirring and pH value was maintained between 5.5 -6.5 respectively.

It has found wide spread use as the basis of a whole range of sacrificial coatings for steel substrate. The metal can be applied by a variety of techniques including metal spraying, cladding, hot-dip galvanising and electrode position [1,2] . As a sacrificial coating under normal temperature and atmospheric condition, zinc provides good protection to underlying steel substrate. However, electrodeposited zinc alloys are gaining industrial importance for similar uses. These are usually of zinc or "Zinc-Iron" alloys.

Zinc coatings are effective in isolating the substrates from the environment and provide sacrificial protection to steel if damage occurs to the coating. However, in some environments the corrosion resistance of pure zinc coating is insufficient to provide long term protection. The corrosion resistance of zinc coating can be improved by making alloy additions and/or by passivation[3].

EXPERIMENTAL:

Zinc dross of impure grade was taken as anode material. Mild steel cathode 2.5X3.5cm were polished with silicon carbide paper up to grade 500. They were degreased, rinsed, dried and kept in dessicator before use. Analytical/laboratory grade chemicals like KCl, NaCl, NH4Cl, HCl, borax Chromic Oxide etc. were used for electrodeposition and corrosion resistance . The surface cleaning before coating is important to avoid surface imperfection on the coated product. After washing, zinc dross anode was kept in electrodeposition cell, parallel to the mild steel sheet acting as cathode at a distance of 25mm with proper adjustment of current and voltage, the coating developed and time taken 30 sec,60 sec,90 sec,120 sec and so on respectively. Electrodeposited zinc coatings were passivated by a conventional process just to reduce oxidation. Salt spray test was carried out, using a neutral salt fog in accordance with ASTM B117 [4]. The coatings were electrodeposited from chloride based bath and the composition of the zinc dross as given below:

<table>
<thead>
<tr>
<th>Specimen</th>
<th>V.H.N.</th>
<th>V.H.N.</th>
<th>V.H.N.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mild steel</td>
<td>385</td>
<td>383</td>
<td>384</td>
</tr>
<tr>
<td>Zinc coated steel</td>
<td>286</td>
<td>258</td>
<td>350</td>
</tr>
</tbody>
</table>

Coating thickness:

Coating thickness of electrode posited zinc coating varied between 5-9 mm. Generally, current density and time were varied to obtain required thickness. Coating thickness was measured by magnetic gauge while micro-hardness of the coating was measured by V.H.N. as shown in Table -I

Atmospheric Exposure Test:
Electrodeposited zinc coated sheet or tube was exposed in the industrial atmosphere at Jamshedpur for a period of one year. Rust appeared on the edges after considerable time period as shown in fig 1 and Table II. The samples were exposed as per IS -5555,1970.

**Table II- Exposure test of zinc coated substrate in Industrial atmosphere at Jamshedpur**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Rating of surface before exposure</th>
<th>Rating of surface after exposure (Period in months)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>4  8  12</td>
</tr>
<tr>
<td>Mild steel sheet</td>
<td>10</td>
<td>9  8  7</td>
</tr>
<tr>
<td>Mild steel tube(out side)</td>
<td>10</td>
<td>9  8  7</td>
</tr>
<tr>
<td>Mild steel tube(in side)</td>
<td>10</td>
<td>10 9 9</td>
</tr>
</tbody>
</table>

**Electrochemical studies :**

The electrodeposited zinc coated sample was used as working electrode and graphite as auxiliary electrode with saturated calomel electrode as reference electrode in potentiostat model 273 EG&G PARC and the data collected by Tafel plot at a scan rate of 2mv/sec at room temperature and surface area of 1cm2was exposed for the test. The corrosion current (Icorr.), OCP and corrosion ratings were determined as shown in table-III

**Table III- Electrochemical test results of Zinc coated substrates in 3.5% NaCl solution**

<table>
<thead>
<tr>
<th>Coated Specimen</th>
<th>OCP (-mv)</th>
<th>Ecorr (-mv)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
</tr>
<tr>
<td>Mild steel sheet</td>
<td>1060</td>
<td>1070</td>
</tr>
<tr>
<td>Mild steel tube</td>
<td>1058</td>
<td>1065</td>
</tr>
<tr>
<td>Mild steel tube(in side)</td>
<td>1062</td>
<td>1070</td>
</tr>
</tbody>
</table>

**Results and Discussion :**

The main features of this process are higher current efficiency and lower cell voltage. The main function of the chloride ions like NaCl, KCl etc in the electrodeposition cell is to increase the conductivity of the solution and decreases the cell voltage [6].

Electrodeposited zinc-iron alloy coatings are applied to steel sheet for corrosion protection of the underlying steel by both a barrier and galvanic protection mechanism. Electrodeposited Zinc-alloy coating is commercially obtained by co-depositing iron and zinc from a sulfate or chloride based aqueous bath. The co-deposition of two metals can lead to supersaturated solid solution and non-equilibrium phases in the electrodeposited material [5,7]. Current density and time were varied to
obtain coating of 5-7 mm thickness. It was observed that during electrode position of Zinc, the anodic efficiency is normally higher than the cathodic efficiency owing to the chemical attack of the solution on the Zn dross anode.

Micro hardness data indicates that the coating is very thin and not so uniform. It may be due to anode impurities [8]. Electrodeposited zinc coating exposed in the industrial atmosphere at Jamshedpur as shown in table II. The rust appeared on the edges of the sample but other surfaces remain intact due to the presence of non-porous, adherent corrosion product on the surface. The corrosion product formed on electrodeposited Zinc coatings are mainly Zn5(CO3)21ZnO, ZnSO4,ZnOHC1 (Zinc chloride hydroxide), Zn4Si2O7(OH)2 (Zincsilicate hydroxide) and ZnOSiO2 as identified by X-ray diffraction.

The reason is the natural protection to steel by zinc itself against corrosion. Potential of zinc is negative to iron and can protect the steel sacrificially even in the presence of pores. Thus thermodynamically zinc is very active compared to iron and in practice it is corroded sacrificially in contact with iron in most of the environments.

Polarisation was carried out in 3.5% NaCl and initial and final value of open circuit potential corrosion potential, rating are indicated in Table III. The electrodeposited zinc coating exhibited more negative potential compared to hot-dip galvanised coating in 3.5%NaCl solution [9]. Maximum cathodic efficiency obtained during the electrodeposition of zinc from zinc dross was 90-91%.Although anodic efficiency was normally more than the cathodic one, it decreased significantly sometime owing to passivation.

Electrodeposited zinc coating was compared with hot dip coating and it was observed that electrode posited zinc coating is more ductile than hot - dip coating because the coating is brittle due to intermetallic compound of Zinc and Fe at the coating interface. The properties of electrodeposited zinc from chloride solution are better than obtained by other methods. The electrogalvanising is simply under the mixed control of charge transfer and diffusion.

CONCLUSIONS:

Electrodeposited zinc coatings are excellent for the protection of steel substrates. The maximum cathodic efficiency was 90 to 91% from zinc dross as anodic material by galvanised/electrochemical route. Electrodeposited zinc coatings are more ductile than hot- dip coating because hot dip coatings are brittle due to formation of intermetallic compounds. The process is free from pollution and economically viable. It has very good corrosion resistance.

5. Acknowledgement :

The authors are thankful to Prof. S.P. Mehrotra, Director, National Metallurgical Laboratory; Jamshedpur for his permission to present and publish the paper.

REFERENCES :

1. O.R.Gabi, Principle of metal surface treatment and protection, 2nd Edition; Pergamon


Fig. 1: Shows industrial exposure test of electro-deposited zinc coating from zinc dross on mild steel sheet at Jamshedpur.