Modeling and microstructural studies on anomalous electrodeposition of zinc-iron alloy

M Kanagasabapathy* & Sobha Jayakrishnan
1Department of Chemistry, Rajapalayam Rajus’ College, Madurai Kamaraj University, Rajapalayam, 626 117, India
2EMFT Division, Central Electrochemical Research Institute, Karaikudi 630 006, Tamilnadu, India

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This study correlates the deposition parameters with the alloy characteristics, through mathematical models based on zinc-iron alloy deposition. Both the partial and transition current densities have been determined. It should be noted that by designing specific models for a given boundary condition, the desired alloy composition can be achieved. The effect of deposition parameters on both cathodic as well as anodic potential and the electrochemical kinetics has also been investigated and the exchange current density values are computed. Effect of deposition rate as well as alloy phase composition over the textural characteristics and hkl planes is also observed.

Keywords: Anomalous electrodeposition, Electrodeposition modeling, Zinc-iron alloy

Among the various alloy electrodeposition processes, zinc alloyed with iron group metals are having greater industrial significance due to its higher corrosion resistance. But this deposition belongs to anomalous deposition, where the electrochemically less noble metal deposits preferentially over more noble metal. Due to this anomalous deposition, precise process control over the formed alloy cannot be established. Though different anomalous deposition mechanisms with contrary views were reported, no literature was available to predict the alloy composition with reference to the given deposition conditions. This study correlates the deposition parameters and alloy composition, through mathematical models with reference to zinc-iron alloy anomalous deposition, since zinc-iron alloy deposit provides three times higher corrosion resistance and has better mechanical properties when compared to zinc coatings. It should be noted that, to get the desired degree of protection, the alloy should contain 15-25 wt % of iron (noted as optimum iron content) and for better paintability, the coating should have 50 wt % of iron.

Experimental Procedure
Electrodeposition of zinc-iron alloy was carried out from sulphate bath. Analar grade chemicals were used. ZnSO₄.7H₂O and FeSO₄(NH₄)2SO₄. 6H₂O (FAS) were used in the bath for the source for zinc and iron respectively. KCl was added to enhance the specific conductance and secondary current distribution of the bath. Disodium salt of EDTA was added to improve the bath stability. Deposition was done over mechanically polished and electro cleaned mild steel panels of size 5.0 cm × 2.5 cm × 0.05 cm, under galvano static conditions by means of three electrode assembly, using a DC regulated power supply (Aplab L3230 model, India). The anode used was electrolytic grade zinc, with the same dimensions to that of cathode. Values of cathodic over potential (ηc) were measured at every 30s at a given cathodic current density (ic) with reference to saturated calomel electrode (SCE) through Luggin probe assembly. Based on the three electrode assembly, potentiostatic studies over glassy carbon electrode were carried out by using Autolab PGSTAT 30 electrochemical analyzer (The Netherlands make). Glassy carbon electrode of area 0.25 cm² (Tokai Carbon Company, Japan) was used as the working electrode. A thin platinum foil of 2.5 cm × 2.5 cm area was used as the counter electrode and saturated calomel electrode was used as the reference electrode. To eliminate the interference of oxygen, bath was purged by passing pure nitrogen for one hour. Bath composition was analyzed by atomic absorption spectrophotometer (VARIANT model SPECTRAA 220 model) and the alloy composition was analyzed by energy dispersive X-ray analyzer (Hitachi S-3000H model), followed by

*Corresponding author.
E-mail: rjpmks@yahoo.com
atomic absorption spectrophotometer after dissolving in 1:1 HNO₃. Composition of the deposited alloy was expressed in weight percentage of iron and denoted as pFe. Micro hardness of the coating was measured in Vicker’s hardness number (VHN) by static indentation method, using Leco micro hardness tester (Model M 400) under the load of 50 g with a deposit thickness of 25 µm. X-ray diffraction patterns were taken by using JEOL PANalytical, X’ pert PRO model, by using Cu Kα (λ = 1.54 Å) radiation. Deposits were scanned between 20° and 80° (2θ) at a rate of 1° min⁻¹. The hkl values of zinc and hkl values of iron were interpreted in accordance with ICDD 34. Morphologies of the deposit were noted by scanning electrons microscope (SEM) (Hitachi S-3000H model), for the required magnification.

Results and Discussion
Effect of Zn²⁺ and Fe²⁺ concentration over the alloy composition

The value of pFe is noted at various current densities (1-8 Adm⁻²) by varying the Zn²⁺ and Fe²⁺ concentration in bath. Similarly, pFe value is noted by varying the concentrations of ZnSO₄·7H₂O at a fixed concentration of FAS (50, 75, 100, 125, 150 and 175 gL⁻¹) in the bath. For all i_c values studied, the iron contents of the bath (Fe_b) and alloy are correlated by models. It is noticed that relatively better deposits with smooth and white appearance occur at 3 Adm⁻². The iron contents of the bath (Fe_b) and alloy (Fe_d) at 3 Adm⁻² are correlated by an approximation Fe_d = exp (k x Fe_b) where ‘k’ is found to be equal to 0.05 ± 0.0025 (Fig. 1).

Table 1—Effect of Zn²⁺ and Fe²⁺ concentrations on alloy composition at 3 Adm⁻²

<table>
<thead>
<tr>
<th>Zn²⁺ and Fe²⁺ content in bath, gL⁻¹</th>
<th>Bath content, gL⁻¹</th>
<th>Fe, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO₄·7H₂O FeSO₄(NH₄)₂SO₄·6H₂O</td>
<td>Zn  Fe  Bath  Alloy</td>
<td></td>
</tr>
<tr>
<td>99 17.6</td>
<td>22.5  2.5  10   1.6</td>
<td></td>
</tr>
<tr>
<td>88 35.1</td>
<td>20.0  5.0  20   2.9</td>
<td></td>
</tr>
<tr>
<td>77 52.7</td>
<td>17.5  7.5  30   5.2</td>
<td></td>
</tr>
<tr>
<td>66 70.2</td>
<td>15.0 10.0  40   8.4</td>
<td></td>
</tr>
<tr>
<td>55 87.8</td>
<td>12.5 12.5  50   13.2</td>
<td></td>
</tr>
<tr>
<td>44 105.3</td>
<td>10.0 15.0  60   24.7</td>
<td></td>
</tr>
<tr>
<td>33 122.9</td>
<td>7.5 17.5  70   40.3</td>
<td></td>
</tr>
<tr>
<td>22 140.4</td>
<td>5.0 20.0  80   62.4</td>
<td></td>
</tr>
<tr>
<td>11 158.0</td>
<td>2.5 22.5  90   86.2</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1—Correlation of Fe % in bath to alloy at 3 Adm⁻²

phenomenon. Iron content of alloy is always lower than the bath composition reference line (CRL). From these studies it can be correlated that, to get a deposit with an optimum iron percent (pFe about 15%) at a cathodic current density of 3 Adm⁻², the bath should contain about 56% iron content. Based on the alloy composition (with optimum iron content), nature and appearance of the deposit, the optimized composition of the standard bath used for the study is taken as ZnSO₄·7H₂O, 80 gL⁻¹; FAS, 160 gL⁻¹; Na₂EDTA, 60 gL⁻¹; and KCl, 50 gL⁻¹. This bath has an iron content of 55.6%.

Effect of current density

The value of pFe, under the given i_c value for the optimized bath has been measured and given in Fig. 2. It increases with increase in value of i_c. For a given current density [i_c(x)], the wt % of iron content of the alloy at a given condition [pFe(x)] is predicted through Lagrange interpolation of irregular intervals. Values of apparent current densities, i_c(1), i_c(2) … i_c(n) and its corresponding wt % of iron content of the alloy pFe(1), pFe(2) … pFe(n) can be correlated by the following mathematical correlation:
Based on this, the value of $p_{Fe}$ for a given $i_c$ value at 30 °C can be correlated by the following polynomial equation $p_{Fe} = -a_i^2 + 40 a_i + 4a$. The determined value of $i_t$ at bath CRL is found to be 14.2 Adm$^{-2}$ and the predicted value is 13.6 Adm$^{-2}$. The effective partial current density values are computed for iron ($i_{Fe}$), zinc ($i_{Zn}$) and hydrogen evolution reaction, HER ($i_{H}$) (Fig. 3).

It is observed that the $i_{Fe}$ value is always lower than $i_{H}$ value for all total current density values. This shows that the overall deposition rate of the iron is lower than the deposition rates of zinc and HER. The value of hydrogen overpotential for iron is about 0.53 V and for zinc it is 0.75 V at a concentration of $[H^+] = 1$ M at 1 Adm$^{-2}$. So, it can be noted that the HER competes with the iron deposition rate rather than with zinc deposition rate. This shows, that the reduction rate of iron is controlled by charge transfer limitations, specifically at low $i_c$ values.

**Electrochemical kinetics of Fe$^{2+}$ deposition**

Tafel plot for variation in Fe$^{2+}$ concentration under galvanostatic conditions is given in Fig. 4. The effect of Fe$^{2+}$ concentration over the change in $\eta_c$ between the $i_c$ values of 1–5 Adm$^{-2}$ at a time duration ($t$) of 10 min is computed and given in Fig. 5. If the concentration of Fe$^{2+}$ in the bath is increased, then the $\eta_c$ values shift more positively. Similarly, studies are carried out under potentiostatic conditions at a scan rate of 10 mV s$^{-1}$ to observe the effect of Fe$^{2+}$ on the
overall deposition rate (Fig. 6). It is observed that in the presence of Fe$^{3+}$, the cathodic peak potential is shifted less negatively during the forward scan. The measured standard equilibrium reduction potential for Fe$^{2+}$ is found to be less negative (–0.199 V) than Zn$^{2+}$ (–0.519 V) with reference to SCE for 1 M metal ion at 30 °C.

But the anodic peak potential shifts more positively and during the reverse scan two anodic peaks are noted. This shows that the alloy dissolution phase takes place under two different potential regions. Zinc rich alloy undergoes anodic dissolution at more negative potential (–0.725 V), whereas iron rich alloy undergoes dissolution at relatively more positive anodic potential (–0.585 V) when compared to pure zinc dissolution potential (–0.748 V). The area under anodic potential (–0.585 V) when compared to pure zinc dissolution potential (–0.748 V). The area under cathodic peak current increased if the concentration of Zn$^{2+}$ 2+ increases if the concentration of Fe$^{2+}$ in the bath is increased, but the anodic dissolution current is not altered significantly. So it is corroborated that the overall cathodic potential reduces due to the kinetic limitations and the charge-transfer controlled deposition process of the Fe$^{2+}$. The effective exchange current density ($i_o$) values are computed. The $i_o$ value is found to be $1.58 \times 10^{-2}$ A dm$^{-2}$ in the absence of FAS and decrease to $1.99 \times 10^{-3}$ A dm$^{-2}$ at a concentration of 160 gpl of FAS in the bath. This shows that the deposition rate of Fe$^{2+}$ is a kinetically hindered process, though its concentration in the bath is quite high.

It is noted that the variation in Zn$^{2+}$ concentration upto 100 gL$^{-1}$ in the bath does not have much significant effect on alloy composition, since from the bath composition analysis it is found that the concentration of Zn$^{2+}$ in bath remains almost constant throughout the study, through the dissolution of anode.

It is observed that the iron content in the alloy decreases either if the bath temperature is increased or if the bath is stirred. So, the deposition of iron is hindered by charge-transfer control process at lower $i_c$ values, whereas the deposition rate of zinc is retarded only by mass-transport limitations at relatively higher $i_c$ values. Though the electrode-electrolyte interface is enriched with Fe$^{2+}$, its deposition rate is impeded due to charge-transfer restrictions and by the higher activation over potential of Fe$^{2+}$ specifically at lower $i_c$ values. So, under this condition, its concentration over potential is lower than the activation over potential.

At higher $i_c$ values, the deposition rate of Zn$^{2+}$ is very high in the initial stages when compared to Fe$^{2+}$ and this leads to rapid depletion of Zn$^{2+}$ ions near the cathode interface. At this phase, the deposition rate of Zn$^{2+}$ is far higher than its diffusion rate and hence its deposition process comes under mass-transfer control. Because of this mass transfer limitations of Zn$^{2+}$ from bulk (without any convection), its concentration at the interface is lowered and this leads to enhance the deposition rate of Fe$^{2+}$, even if Fe$^{2+}$ has a lower $i_o$ value than zinc. This enhances the concentration over potential of the Zn$^{2+}$, although it has relatively lower activation over potential than Fe$^{2+}$. This diffusion control limitations of Zn$^{2+}$ can be reduced by external convection such as bath stirring or by increasing the bath temperature. By means of induced convection, the cathode interface is quickly enriched with Zn$^{2+}$ and so the deposition rate of iron can be lowered again by the resumption of zinc deposition. At 50 °C, the $p_{Fe}$ value can be correlated to $i_c$ by the following approximation with an $R$ value of 0.9965 ($p_{Fe} = 4.5 i_c + 0.75$).

**Role of crystal field stabilization energy in anomalous deposition**

Fe$^{2+}$ ion has d$^6$ configuration and it has to acquire six pair of electrons, whereas Zn$^{2+}$ has d$^{10}$ configuration and hence it has to gain four pair of electrons from ligands to have an EAN (effective atomic number) value of $^{36}$Kr. In Fe$^{2+}$, the hybridization involved is either d$^2$sp$^3$ or sp$^3$d$^2$ and so hexa dentate complexes are formed. In Zn$^{2+}$, the hybridization involved is predominantly sp$^3$ rather than dsp$^2$ and so tetrahedral complexes are formed rather than square planar. The degenerate five 'd'
orbitals of Fe$^{2+}$ undergoes splitting and form three $t_{2g}$ orbitals of lower energy, with each $-4$ Dq value and two $e_g$ orbitals of higher energy, with each $+6$ Dq value. In Fe$^{2+}$ by the presence of weak field ligands, octahedral crystal field stabilization energy ($\Delta_{o,H}$) is lower than the pairing energy of electrons and so high spin complexes are possible. And in a strong ligand field, the octahedral crystal field stabilization energy ($\Delta_{o,L}$) is higher than the pairing energy of electrons and so low spin complexes are possible. The degree of stabilization energy in both weak and strong ligand field can be easily calculated and given as:

For high spin complexes, value of Fe$^{2+}\Delta_{o,H} = (e_g)^2 - (t_{2g})^4 = 4$ Dq

For low spin complexes, value of Fe$^{2+}\Delta_{o,L} = (e_g)^0 - (t_{2g})^6 = 24$ Dq

The degenerate five ‘d’ orbitals of Zn$^{2+}$ undergoes splitting in tetrahedral field and form three $t_2$ orbitals of higher energy, with each $+4$ Dq value and two $e$ orbitals of lower energy, with each $-6$ Dq value. Due to the d$^{10}$ configuration of Zn$^{2+}$, the pairing energy of electrons is less significant and $\Delta_t$ in Zn$^{2+}$ is zero. So, in presence of both high spin as well as low spin complexes the tetrahedral field stabilization energy ($\Delta_t$) for Zn$^{2+}$ is given as: Zn$^{2+}\Delta_t = (t_2)^6 - (e)^4 = 0$ Dq.

So, the magnitude of stabilization from CFSE values is in the order: Fe$^{2+}\Delta_{o,L} > Fe^{2+}\Delta_{o,H} > Zn^{2+}\Delta_t$.

Due to the large number of ligands in octahedral field than in tetrahedral field, the ligands can approach easily towards Fe$^{2+}$ (both in low spin and high spin) than Zn$^{2+}$. This leads to increase the charge density around Fe$^{2+}$ and thus promotes the stability of the complex formed. In aqueous solutions or in presence of complexants, Fe$^{2+}$ undergoes hexadentate coordination, either by low spin or high spin complex formation, depends on the ligand field. But Zn$^{2+}$ undergoes tetradyentate coordination complexes alone, irrespective of the ligand field. Hence, the relative stability of Fe$^{2+}$ complexes is higher than Zn$^{2+}$ complexes under a given ligand field. So, the influence of electric field is significant than the ligand field on Zn$^{2+}$, when compared to Fe$^{2+}$. This ligand field effect leads to retard the deposition rate of Fe$^{2+}$.

**X-ray diffraction studies**

XRD patterns of the deposits obtained by varying the concentration of Fe$^{2+}$ and $i_c$ values are given in Fig. 7. The computed empirical formula is also indexed. Generally, the pyramidal textural intensity is

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![X-ray diffraction patterns of the deposits](image-url)
significant compared to prismatic intensity. For zinc rich deposits 002 basal plane has significant textural intensity. Similarly the (101) peak is present almost in all deposits with significant intensity. In this study, the peak noted at the 2θ value of 77° is indexed to (004) plane. This plane has not been reported in the previous studies. At 2 Adm⁻² the observed intensity is relatively higher. (200)α peak for iron is noted for deposits obtained above 2 Adm⁻² at a θ value of 32.514°. For the alloy with higher iron content, the (100)α peak for iron is noted at a θ value of 22.3385°, but 004 and 112 plane intensities are diminished.

A shift in crystallographic planes is noted towards higher or lower 2θ values with the change in iron content of the alloy. If the iron content in the alloy is increased, both 002 and 102 peaks shift to higher 2θ, whereas 100 peak shifts to lower 2θ. But irrespective of p Fe, the shift is not significant for 101 plane. This indicates that the hcp lattice gets distorted, if the iron content is increased. Peak broadening due to internal lattice strain is not found from the observed full width at half maxima (FWHM) values. This shows that the adherent and strain free deposits are obtained under the conditions studied.

The alloy formed belongs to intermediate phase type since the crystal structures of both metals are not same and atomic volumes of iron and zinc differ about 20%. The mutual solubility of atoms during alloy formation is limited. Based on Hume-Rothery's rule this alloy belongs to inter metallic compounds of variable composition and may be classified as ‘Electron compounds’. So, the alloy formed is in between an ideal solid solution and a chemical compound. In the hcp lattice the iron atom can easily substituted along the axial plane rather than basal plane. Since the basal plane has higher packing density with six atoms, the axial plane has only three atoms. Further studies are being carried out by the authors to observe the effect of substitution of iron atoms in the geometrical lattice parameters and other crystallographic textural properties.

Morphological studies

The morphology of the deposits obtained at different i c values and with different iron contents are presented in Fig. 8. It is observed that the morphology

![Fig. 8—SEM images of the deposits obtained at different i_c values](image-url)
of the deposit changes with the increase in iron content. Zinc rich alloys such as Fe$_5$Zn$_{73}$, Fe$_{14}$Zn$_{69}$ and Fe$_8$Zn$_{10}$ have distorted hexagonal structure. Alloys with optimum iron content such as Fe$_5$Zn$_{14}$, Fe$_{14}$Zn$_{13}$, Fe$_{16}$Zn$_{20}$ and Fe$_8$Zn$_{69}$ have triangular pyramidal morphology. The alloys such as Fe$_5$Zn$_{10}$ has stacked rectangular platelet morphology.

Relatively smooth, white and compact deposit with fine grains are observed at 3 Adm$^{-2}$. So, the deposition is under kinetic control and the rate of deposition is relatively faster. This indicates that the overall deposition rate is predominantly controlled by charge-transfer processes rather than mass-transfer processes. Reduction in the crystallite size at 3 Adm$^{-2}$ shows that the nucleation rate is higher than the grain growth rate. At lower current densities such as 1 Adm$^{-2}$, the grain growth rate is significant since both the deposition rate and the nucleation rate are slower. Above 5 Adm$^{-2}$, coarser deposits with grey finish are observed. At higher current densities (above 5 Adm$^{-2}$), the overall deposition rate is significantly influenced by mass-transfer limitations rather than charge-transfer limitations. So, the deposition rate was relatively higher than the uniform nucleation rate and ad-atom formation rate.

Based on these studies, it is observed that at lower iron content (up to 10%), ‘Γ’ phase is noted and with the increase in iron content, ‘I’ phase is formed. Formation of these two phase structures can be explained through the deposition kinetics. At lower current densities, the mass transport limitations for Zn$^{2+}$ are not significant when compared to charge-transfer restrictions of Fe$^{2+}$. So, the overall grain growth rate is higher than the nucleation rate and the deposition of zinc ad-atoms takes place gradually, leads to the formation distorted hcp ‘η’ phase. But, at higher current densities, the overall deposition rate is limited by diffusion control processes. Due to this, the deposition rate of zinc is very fast when compared to its diffusion rate. At this stage, the electrode interface is enriched with Fe$^{2+}$ due to the quick depletion of Zn$^{2+}$ and so the kinetic control limitations of Fe$^{2+}$ can be reduced significantly. Hence, the iron ad-atoms are adsorbed over the previously formed hcp ‘η’ phase and leads to the formation of ‘Γ’ phase.

The micro hardness of the deposits with these two phases has been measured. The hardness of the deposits with ‘η’ phase is found to be about 120 VHN and it increases to about 168 VHN for deposits with ‘Γ’ phase. This indicates that relatively harder and denser ‘Γ’ phase is formed in the deposits with an optimum iron content and so the other mechanical properties such as abrasion resistance and tensile strength can also be improved.

**Conclusion**

By designing specific models for a given boundary condition, the alloy composition can be controlled though the electrodeposition proceeds anomalously. Relatively smooth and compact deposit with optimum iron content as per industrial standards can be obtained at 3 Adm$^{-2}$ from the optimized bath taken. Deposition is prevailed mainly through charge-transfer control process for iron under low cathodic current density values. But zinc deposition is hindered by mass-transfer control process particularly at high cathodic current density values. The (101) hcp plane is present in almost all deposits with significant intensity. Both η and Γ phases are present and (200) peak for iron is noted. Inter metallic compounds of variable composition such as Fe$_5$Zn$_{73}$, Fe$_{14}$Zn$_{14}$, Fe$_9$Zn$_{69}$, Fe$_2$Zn$_{133}$, Fe$_{16}$Zn$_{13}$, Fe$_{18}$Zn$_{20}$, F$_{18}$Zn$_{61}$, Fe$_2$Zn$_{10}$ are noted under the deposition conditions studied.

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