Chapter IV

4 Zinc Cobalt co-deposition

Electroplating Zn-Co is relatively a novel process. Since 1970s many academic papers and patents on this subject have been reported. This deposit exhibits substantial improvement in corrosion protection compared with pure zinc. Zinc-Cobalt alloy plating process based on an acid chloride electrolyte has been in commercial operation for over years and has gained wide acceptance in many countries. In the present work zinc-cobalt deposits are obtained under air agitation and sonication. The deposits are then analyzed to find changes in the morphology, composition and the crystallinity. Following is the results thus obtained.

4.1 X-ray analysis

Figure 4.1 to 4.5 shows the X-ray diffractograms of the zinc cobalt co deposits obtained under air-agitated condition and at plating current densities from 1 to \(5A/dm^2\). The highest reflection intensity for the deposits appears between 41.82° and 43.975°. Figures 4.6 to 4.10 are the X-ray diffractograms of the deposits obtained under sonicated conditions.
Figure 4.1 X-ray diffractogram of deposit obtained under air agitation plating current density = 1 A/dm²

Figure 4.2 X-ray diffractogram of deposit obtained under air agitation plating current density = 2 A/dm²

Figure 4.3 X-ray diffractogram of deposit obtained under air agitation plating current density = 3 A/dm²
Chapter IV Electrodeposition of Zinc-Cobalt Alloy

Figure 4.4 X-ray diffractogram of deposit obtained under air agitation
plating current density = 4 A/dm²

Figure 4.5 X-ray diffractogram of deposit obtained under air agitation
plating current density = 5 A/dm²

Figure 4.6 X-ray diffractogram of deposit obtained under
sonicated condition
plating current density = 1 A/dm²
Figure 4.7  X-ray diffractogram of deposit obtained under
sonicated condition
plating current density = 2 A/dm$^2$

Figure 4.8  X-ray diffractogram of deposit obtained under
sonicated condition
plating current density = 3 A/dm$^2$

Figure 4.9  X-ray diffractogram of deposit obtained under
sonicated condition
plating current density = 4 A/dm$^2$
Figure 4.10  X-ray diffractogram of deposit obtained under sonicated condition
plating current density = 5 A/dm²

The highest reflection intensity for these deposits appears between 42.47° and 43.93°. In case of air-agitated deposit, intensity of the peak with highest reflection intensity decreases with increase in plating current density. In case of sonicated deposits, intensity of the peak remains almost constant for all current densities. X-ray diffractograms show difference between the diffractograms of air-agitated deposit and sonicated deposit, indicating that the coatings are entirely different. There are two more peaks, which were very significant for sonicated deposits, between (i) 35.445° and 36.5° and (ii) 38.245° and 39.28°. Two more peaks were also found between the range 53.69°-
45.48° and the second range is between 68.125°-70.2°. The peak values given here are the maxima and minima though the peak position varies for a particular plating current density. These four peaks were not observed with the air-agitated deposits. This difference indicates that the deposit obtained under sonicated deposits undergo a different mechanism of deposition. Further in order to find the origin of these four peaks, the standard X-ray diffractograms of zinc and cobalt metals were compared with the deposits obtained by both the conditions.

Figures 4.11 and 4.12 gives the comparison of the standard zinc diffractogram and the deposits obtained at various plating current densities of air-agitated and sonicated deposits respectively. The deposit obtained under air-agitated condition does not match with the standard zinc metals diffractogram, whereas the sonicated deposits shows similarities indicating the presence of free zinc metal in the deposit.

The four peaks, which were, mentioned earlier shows a close match to that of the zinc metal. Following table 4.1 gives the values of the 2θ, which were close to the standard peaks of the zinc metal. The 2θ values show the close proximity of the coatings to have zinc metal as a separate phase in the deposit. With increase in the plating current density the number of matching peaks decreases indicating the disappearance of the free zinc metal. This shows that at lower plating current density zinc
deposits as an independent phase, which later on tends to form a solid solution with the cobalt, which is co-deposited with zinc.

Figure 4.11   Comparison of X-ray diffractograms of deposits obtained under air agitated condition and at various plating current density with standard zinc metal, vertical lines represent zinc metal

Figure 4.12   Comparison of X-ray diffractogram of the deposits obtained under sonication and at various plating current densities with that of the standard zinc metal, straight lines represent zinc
Table 4.1  Comparison of 2θ values of deposits obtained under sonicated condition and at various plating current density with that of the standard zinc metal

<table>
<thead>
<tr>
<th>Zinc standard, 2θ values (degrees)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 A/dm²</td>
<td>2 A/dm²</td>
<td>3 A/dm²</td>
<td>4 A/dm²</td>
<td>5 A/dm²</td>
</tr>
<tr>
<td>36.29</td>
<td>36.54</td>
<td>35.86</td>
<td>35.71</td>
<td></td>
<td>36.36</td>
</tr>
<tr>
<td>38.99</td>
<td>39.28</td>
<td>38.29</td>
<td>38.25</td>
<td>38.245</td>
<td>39</td>
</tr>
<tr>
<td>43.23</td>
<td>43.405</td>
<td>42.54</td>
<td>43.93</td>
<td>43.93</td>
<td>43.24</td>
</tr>
<tr>
<td>54.33</td>
<td>54.48</td>
<td>53.77</td>
<td>53.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70.05</td>
<td>70.21</td>
<td></td>
<td></td>
<td></td>
<td>70.35</td>
</tr>
<tr>
<td>77.02</td>
<td></td>
<td>77.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>82.09</td>
<td>82.53</td>
<td></td>
<td>81.61</td>
<td>82.22</td>
<td></td>
</tr>
<tr>
<td>83.76</td>
<td>84.24</td>
<td>84.47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>89.90</td>
<td>88.88</td>
<td>88.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>109.14</td>
<td></td>
<td></td>
<td>108.78</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Following table 4.2 shows the major peaks for zinc standard metal and the observed 2θ values for the air-agitated deposit. When 2θ values of the deposits obtained under air-agitated conditions where compared with the standard zinc metal’s major peaks no such resemblance could be observed. Form the table it is clear that the deposition assisted by air agitation leads to a coating with less or no free zinc metal. Also it is clear that the deposit becomes apparent that the increase in current leads to a
deposit with less free zinc metal. Thus increase in agitation leads to the
deposition with less nobler metal in the coating as a separate phase.

Table 4.2  Comparison of 2θ values of deposits obtained
under air-agitated condition and at various
plating current density with that of the standard
zinc metal

<table>
<thead>
<tr>
<th>Zinc standard, 2θ values (degrees)</th>
<th>2θ values (degree) of deposits obtained under air-agitated conditions and at current densities:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 A/dm²</td>
</tr>
<tr>
<td>36.29</td>
<td></td>
</tr>
<tr>
<td>38.99</td>
<td></td>
</tr>
<tr>
<td>43.23</td>
<td></td>
</tr>
<tr>
<td>54.33</td>
<td></td>
</tr>
<tr>
<td>70.05</td>
<td></td>
</tr>
<tr>
<td>77.02</td>
<td>77.905</td>
</tr>
<tr>
<td>82.09</td>
<td>81.73</td>
</tr>
<tr>
<td>83.76</td>
<td></td>
</tr>
<tr>
<td>89.90</td>
<td></td>
</tr>
<tr>
<td><strong>No Match</strong></td>
<td></td>
</tr>
</tbody>
</table>

When 2θ values of standard cobalt is compared with the
measured 2θ values of the deposits, both air-agitated and sonicated
deposits do not show any inclination towards free cobalt metal. Table 4.3
and 4.4 show the major peaks for standard cobalt metal and the
observed 2θ value for the sonicated and air-agitated deposit.
### Table 4.3
Comparison of $2\theta$ values of deposits obtained under sonicated condition and at various plating current density with that of the standard cobalt metal

<table>
<thead>
<tr>
<th>Cobalt standard, $2\theta$ values (degrees)</th>
<th>$2\theta$ values (degree) of deposits obtained under sonicated conditions and at current densities:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1, A/dm^2$</td>
</tr>
<tr>
<td>41.68</td>
<td>36.21</td>
</tr>
<tr>
<td>44.76</td>
<td></td>
</tr>
<tr>
<td>47.57</td>
<td></td>
</tr>
<tr>
<td>62.73</td>
<td></td>
</tr>
<tr>
<td>75.95</td>
<td>77.90</td>
</tr>
<tr>
<td>84.19</td>
<td>81.73</td>
</tr>
<tr>
<td>90.60</td>
<td></td>
</tr>
<tr>
<td>92.52</td>
<td></td>
</tr>
<tr>
<td>94.72</td>
<td></td>
</tr>
<tr>
<td>98.71</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4.4
Comparison of $2\theta$ values of deposits obtained under air-agitated condition and at various plating current density with that of the standard cobalt metal.

<table>
<thead>
<tr>
<th>Cobalt standard, $2\theta$ values (degrees)</th>
<th>$2\theta$ values (degree) of deposits obtained under air-agitated conditions and at current densities:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1, A/dm^2$</td>
</tr>
<tr>
<td>41.68</td>
<td>42.13</td>
</tr>
<tr>
<td>44.76</td>
<td></td>
</tr>
<tr>
<td>47.57</td>
<td></td>
</tr>
</tbody>
</table>
Figures 4.13 and 4.14 show the comparison of the X-ray diffractograms of the deposits obtained at various plating current density with the standard cobalt metal’s diffractogram.

**Cluster size calculation**

Cluster size of the deposits were calculated as discussed in chapter 3 under X-ray analysis, and the values are plotted against plating current density as shown in Figure 4.15 and 4.16 for sonicated and air-agitated deposits. Sonicated batches show almost uniform cluster size until 3 A/dm², and cluster size calculated at 4 shows the maximum value and 5 A/dm² shows a decrease in the value. In the case of the air-agitated
Chapter IV Electrodeposition of Zinc-Cobalt alloy

Figure 4.13  Comparison of X-ray diffractogram of the deposits obtained under sonication and at various plating current densities with that of the standard cobalt metal (straight lines represent cobalt)

Figure 4.14  Comparison of X-ray diffractograms of deposits obtained under air agitated condition and at various plating current density with standard cobalt metal (vertical lines represent cobalt metal)
deposits, there is a gradual increase in the value of cluster sizes. Like the sonicated deposits, air-agitated deposits also show a similar pattern at plating current density of 4 and 5 A/dm$^2$.

![Graph showing variation of cluster size with plating current density for deposits obtained under sonicated condition.](image)

Figure 4.15  Variation of cluster size with plating current density for deposits obtained under sonicated condition.

Ramadan et.al. [87] pointed out that the cluster size calculated by this method results in smaller value than those calculated from SEM, due to coherent diffraction domains are smaller than average size from direct observation. Based on this reason SEM and AFM scans were used to study the surface morphology of the coating.
Figure 4.16  Variation of cluster size with plating current density for deposits obtained under air agitated condition.

4.2 EDAX results

EDAX was done in order to find the elemental compositions of the deposit and it was done as described in chapter II under the sub section EDAX. Cobalt and Zinc were the main constituents of the deposit. Figure 4.17 to 4.21 shows the EDAX results of the deposit obtained under air-agitated condition and at plating current densities 1 to 5 A/dm² respectively. Plots of the energy (KeV) versus CPS for deposits obtained at 3, 4, 5 A/dm² has Fe in the deposit apart from the two other major
constituents, this could be from the substrate, which is mild steel, and hence this peak is not accounted for any analysis.

Figure 4.17  EDAX results of Zinc-Cobalt deposit obtained at 1 A/dm² under air agitated condition

Figure 4.18  EDAX results of Zinc-Cobalt deposit obtained at 2 A/dm2 under air agitated condition
Figure 4.19  EDAX results of Zinc-Cobalt deposit obtained at 3 A/dm² under air agitated condition

Figure 4.20  EDAX results of Zinc-Cobalt deposit obtained at 4 A/dm² under air agitated condition
Figure 4.21  EDAX results of Zinc-Cobalt deposit obtained at 5 A/dm² under air agitated condition

The composition of the deposits obtained under air-agitated conditions were tabulated in the table 4.5, composition is being given in terms of element percentage.

Table 4.5  Element percentage of Co and Zn in the deposit obtained under air-agitated condition and at various current densities.

<table>
<thead>
<tr>
<th>Plating current density (A/dm²)</th>
<th>Element percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cobalt</td>
</tr>
<tr>
<td>1</td>
<td>15.34</td>
</tr>
<tr>
<td>2</td>
<td>10.93</td>
</tr>
</tbody>
</table>
According to D.E. Hall [17] in case of a deposit to be anomalous, the concentration of the less noble metal should decrease with increase in plating current density. The obtained EDAX results shows an increase in the concentration of the less noble metal, zinc with increase in plating current density. Both Shears [88] and Zhang et.al. [89] reported that the increase in plating current density resulted in increase in cobalt concentration. This is not in accordance with the obtained results.

Higashi et.al. [12] has proposed a mechanism to explain the anomalous deposition of zinc cobalt co deposition, which says hydroxide film formed at the surface of the cathode results in increased concentration of the zinc in the deposit thereby suppressing the cobalt ion from being deposited. Recent work by Horkans [14] also supports the increase in concentration of the zinc metal in the deposit with increase in current. Figure 4.22 shows the relation between the current density and the concentration of the more noble metal (cobalt) in the deposit obtained.
<table>
<thead>
<tr>
<th>Plating current density (A/dm²)</th>
<th>Element percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cobalt</td>
</tr>
<tr>
<td>3</td>
<td>11.33</td>
</tr>
<tr>
<td>4</td>
<td>1.89</td>
</tr>
<tr>
<td>5</td>
<td>3.86</td>
</tr>
</tbody>
</table>

According to D.E. Hall [17] in case of a deposit to be anomalous, the concentration of the less noble metal should decrease with increase in plating current density. The obtained EDAX results shows an increase in the concentration of the less noble metal, zinc with increase in plating current density. Both Shears [88] and Zhang et.al. [89] reported that the increase in plating current density resulted in increase in cobalt concentration. This is not in accordance with the obtained results.

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under air-agitation. Figure 4.23 shows the concentration of the less noble metal (zinc) in the deposit obtained under air-agitation.

![Graph showing Cobalt Concentration vs. Plating current density](image)

**Figure 4.22** Plating current density versus Cobalt concentration in the deposit obtained under air agitated condition.

![Graph showing Zinc Concentration vs. Plating current density](image)

**Figure 4.23** Plating current density versus Zinc concentration in the deposit obtained under air agitated condition.
Figure 4.24  EDAX results of Zinc-Cobalt deposit obtained at 1 A/dm$^2$ under sonicated condition

Figure 4.25  EDAX results of Zinc-Cobalt deposit obtained at 2 A/dm$^2$ under sonicated condition
Figure 4.26  EDAX results of Zinc-Cobalt deposit obtained at 3 A/dm² under sonicated condition

Figure 4.27  EDAX results of Zinc-Cobalt deposit obtained at 4 A/dm² under sonicated condition
Figure 4.28 EDAX results of Zinc-Cobalt deposit obtained at 5 A/dm² under sonicated condition

Figures 4.24 to 4.28 shows the EDAX shows the results for the deposits obtained at plating current density of 1 to 5 A/dm² respectively of sonicated deposits.

In this case also the energy versus CPS plot shows the presence of Fe in the deposit which is again from the substrate, both air-agitated and sonicated deposits shows the presence of Fe and the reason for this will be discussed under the forthcoming sections on surface morphology. The concentration of the more noble metal (cobalt) initially decreases with increase in current density up to 3 A/dm² after which the concentration increases and hence the concentration of the less noble metal follow the inverse of the trend as that of the cobalt. Figures 4.29
and 4.30 show the plot of concentration of cobalt and zinc versus the plating current density respectively. This is in accordance with the results obtained from the X-ray diffractograms, as discussed in section 4.1 under X-ray analysis. The deposition assisted by sonicated results in the deposition of zinc metal as a separate phase. Figure 4.31 shows the general trend in the concentration change of zinc with plating current density. Figures 4.32 and 4.33 show the comparison between the concentration of the zinc and cobalt obtained by both the processes.

![Graph showing concentration of cobalt versus plating current density for the deposits obtained under sonicated condition.](image)
Figure 4.30 Concentration of zinc versus plating current density for the deposits obtained under sonicated condition.

Figure 4.31 General trend in the change in concentration of zinc in the deposits obtained under sonicated condition at various plating current densities. Dashed lines indicate the trend.
Figure 4.32  Comparison of zinc concentration in the deposits obtained by air-agitation and sonicated conditions at various plating current densities.

Figure 4.33  Comparison of cobalt concentration in the deposits obtained by air-agitation and sonicated conditions at various plating current densities.
While EDAX results showed the concentration of the cobalt and zinc as individual element, X-ray diffractograms showed the crystalline property of the deposit. In following sections SEM and AFM analysis are presented to study the morphological differences between the deposits obtained air-agitated and sonicated method.

4.3 SEM analysis

Figures 4.34 to 4.38 shows the SEM micrograph for the deposits obtained under air-agitated conditions at plating current density 1 to 5 $A/dm^2$ respectively. In Figure 4.36 the hexagonal crystal faces are very clear and prominent indicating that the deposit obtained is completely crystalline which is in accordance with the X-ray diffractogram (Figure 4.1) for the deposit obtained at the same current density. X-ray diffractogram of the deposit obtained at 1 $A/dm^2$ indicates a high degree of crystalinity. When the plating current density is increased there is a loss in crystalinity as shown in Figure 4.35 to 4.38, and a transition takes place from nodular to fine needle like deposit. The X-ray diffractograms where the intensity of the peak with highest reflection intensity decreases with increase in plating current density as a result of decrease in crystalinity of the deposits again shows this difference. Figure 4.36 shows the SEM micrograph of the deposit obtained at 3 $A/dm^2$, at this plating current density the deposit has attained a fine grain structure and the visual examination of the micrograph reveals that the spheres are of almost
visual examination of the micrograph reveals that the spheres are of almost

Figure 4.34 SEM micrograph of Zinc-Cobalt deposit obtained at plating current density of 1 A/dm² under air-agitated condition.

Figure 4.35 SEM micrograph of Zinc-Cobalt deposit obtained at plating current density of 2 A/dm² under air-agitated condition.
Figure 4.36  SEM micrograph of Zinc-Cobalt deposit obtained at plating current density of 3 A/dm² under air-agitated condition.

Figure 4.37  SEM micrograph of Zinc-Cobalt deposit obtained at plating current density of 4 A/dm² under air-agitated condition
uniform dimensions which is comparable with the results published by short et.al. [36] they reported that this fine grain structure was obtained when the cobalt concentration in the deposit is 10.7%. The EDAX results of this deposits shows the cobalt concentration is 11.2% which is in agreement with the published results. The deposit obtained at plating current density of $4\,A/dm^2$ (Figure 4.37) shows whiskers like growth around the nodules and the coating seems to be very porous. Visual examination of the deposit shows the formation of the dendrites or holes in the coating and the coating had lost its aesthetic appeal. This whisker formation is because of the high deposition rate. Which can be seen in
SEM micrograph of the deposit obtained at $5\text{A}/\text{dm}^2$ (Figure 4.38) where the nodules were not present and the deposit has attained flake like structure perpendicular to the substrate. The dark areas found in the micrograph were from the mild steel substrate.

Figure 4.39 to 4.43 shows the SEM micrographs of the deposit obtained under sonicated condition at plating current densities 1, 2, 3, 4, $5\text{A}/\text{dm}^2$ respectively. In contrast to the deposit obtained at $1\text{A}/\text{dm}^2$ under air-agitated condition, the deposit obtained under sonicated condition at the same plating current density shows no crystalline material. Instead the deposits were like cluster of needles as shown in the Figure 4.37. Close examination of the deposit at higher magnification (Figure 4.42) reveals that each needle of the cluster has a sphere with three or four rods protruding out of the sphere., thus forming a network like structure. At certain spot dumbbell like particulate could be seen, which could be because of the phase separation. The sphere at the center could be because of the clusters of free zinc metal and the small spheres at the end of the needles could be because of the cobalt in the deposit. This assumption was based on the individual elements atomic radius, cobalt (atomic radius = 1.253Å) being smaller than zinc (atomic radius = 1.332Å). The presence of free zinc metal in the deposit is proved by the X-ray diffractograms, where the $2\theta$ values of standard zinc are close to the $2\theta$ values of the deposits given in table 4.2. When the plating current
density is increased the nodular structure changes to spherical particles. Figures 4.38 to 4.41 show this change, except the deposit obtained at $3 \text{A/} \text{dm}^2$ the other deposits follow this trend.

Figure 4.39 SEM micrograph of Zinc-Cobalt deposit obtained at plating current density of 1 A/\text{dm}^2 under sonicated condition.
Figure 4.40  SEM micrograph of Zinc-Cobalt deposit obtained at plating current density of 2 A/dm² under sonicated condition.

Figure 4.41  SEM micrograph of Zinc-Cobalt deposit obtained at plating current density of 3 A/dm² under sonicated condition.
Figure 4.42 SEM micrograph of Zinc-Cobalt deposit obtained at plating current density of 4 A/dm² under sonicated condition.

Figure 4.43 SEM micrograph of Zinc-Cobalt deposit obtained at plating current density of 5 A/dm² under sonicated condition.
4.4 AFM analysis

10X10μm scan of the deposits obtained under air-agitated condition at various plating current densities are shown in figures 4.44 to 4.48. Crystal faces shown by the SEM micrograph of the deposit obtained by air agitation at current density 1A/dm² (Figure 4.34) are displayed by the AFM scans in Figure 4.44. AFM scans bring out the information, which are not shown by the SEM micrograph. Even at higher magnification SEM micrograph did not show the finer surface characteristics like AFM. In figure 4.44 the roughness along each face of the crystal can be seen and this finer information is missing in SEM micrograph due to the restriction of two-dimensional view. The same AFM scan shows growth of the crystal perpendicular to the surface of the substrate. Transition from crystalline deposit to cluster formation is shown by SEM micrographs only at 2A/dm². But the AFM scan of the deposit obtained at 1A/dm² shows the onset of the cluster formation. Figure 4.45 shows the AFM scan for the deposit obtained at 2A/dm² under air-agitated condition. The long continuos lines seen in the figure is the scan line and it should not be mistaken as a part of morphology. This figure shows the fine granular structure on the surface but still the deposit grows in the direction perpendicular to the substrate.
Figure 4.44  AFM scan of Zinc-Cobalt deposit obtained at 1 $A/dm^2$ under air-agitated condition.
Figure 4.45  AFM scan of Zinc-Cobalt deposit obtained at 2 $A/dm^2$ under air-agitated condition.
Figure 4.46  AFM scan of Zinc-Cobalt deposit obtained at 3 $A/dm^2$ under air-agitated condition.
Figure 4.47  AFM scan of Zinc-Cobalt deposit obtained at $4 \text{ A/dm}^2$ under air-agitated condition.
Figure 4.48  AFM scan of Zinc-Cobalt deposit obtained at 5 $A/dm^2$ under air-agitated condition.
Figure 4.46 shows the AFM scan of the deposit obtained at $3 \text{A/dm}^2$ obtained under air-agitated condition. It shows the growth of the pillars close to each other so as to look like a plate growing perpendicular to the substrate. Individual plates were parallel and they had grown close to each other resulting in a big cluster like structure. The spherical bead like structure shown by the SEM micrograph for the same deposit (Figure 4.36), is actually a pillar like growth of the deposit. From the SEM micrograph of the deposit, it was presumed that the coating is of spherical in nature but the AFM scan shows that the coating is still continuos and it is like few plates placed closed to each other. Figure 4.47 shows the AFM scan for the deposit obtained at a plating current density of $4 \text{A/dm}^2$. The needle like structure as observed in the SEM micrograph (Figure 4.37) can be seen with the AFM scan also but the structure is finely resolved by the AFM scan. The plate like structure as observed in other deposits continues in this also. The only difference is the plate like structure did not continue to form the deposit like the coating obtained in the earlier case but got terminated and attained a real pillar like growth with each pillar being the packing of few plates grown close by. When the plating current density is increased to $5 \text{A/dm}^2$ deposit ended up in bigger clusters and the plate like structure is similar to the one observed from the SEM micrograph (Figure 4.38). AFM scan of the same shows the individual plates grown next to each other and forming a individual plates grown next to each other and forming a individual cluster
and is shown in Figure 4.48. This particular scan shows clearly the formation of the individual needle which combines to form a plate and in turn continues to grow together resulting in a cluster. In all the cases the sides of the individual crystal is inclined at a particular angle to the surface. This angle of inclination increases with increase in plating current density, which gives the information that the coating becomes more porous or discontinuous with increase in plating current density.

Following figures 4.49 to 4.55 shows the AFM scans for the deposits obtained under sonicated conditions at plating current densities 1 to $5\,\text{A/dm}^2$ respectively. The AFM scan of the deposit obtained at $1\,\text{A/dm}^2$ (Figure 4.49) shows that the deposit is of pillar like structure tapering away from the surface. This trend is found to be common with the deposits obtained under sonication. With increase in plating current density the compactness of the coating is increased. Figure 4.55 shows the AFM scan for the deposit obtained at $5\,\text{A/dm}^2$ which shows a long stretch of wall like growth proving the assumptions made earlier. From the AFM scan it is clear that the coating obtained under sonicated conditions gives a non-uniform coating.
Figure 4.49  AFM scan of Zinc-Cobalt deposit obtained at $1 \text{A/dm}^2$ under sonicated condition.
Figure 4.50  AFM scan of Zinc-Cobalt deposit obtained at 2 A/dm$^2$ under sonicated condition.
Figure 4.51  AFM scan of Zinc-Cobalt deposit obtained at 3 $A/dm^2$ under sonicated condition.
Figure 4.52 AFM scan of Zinc-Cobalt deposit obtained at 4 \( A/dm^2 \) under sonicated condition.
Figure 4.53  AFM scan of Zinc-Cobalt deposit obtained at 4 $A/dm^2$
under sonicated condition.
4.5 Open circuit potential measurement

The open circuit potential measurement was done for both air-agitated and sonicated zinc cobalt deposits as described in chapter II. The potential measured after 1 hr of immersion was plotted against the plating current density and the cobalt content for these deposits.

![Graph showing potential vs. plating current density](image)

**Figure 4.56** Measured open circuit potential after 1 hour versus plating current density of the deposits obtained under air-agitated condition

Figure 4.56 shows the plot of the potential measured after 1 hr of immersion versus the plating current density of the deposit obtained under air-agitated condition. The deposit obtained at 2 A/dm² registered
the highest potential when compared to the deposits obtained at other current densities. With increase in plating current density the open circuit potential reduced and it reached the substrate's open circuit potential at $5 \text{A/dm}^2$.

EDAX results show that the deposit obtained at $1 \text{A/dm}^2$ contains 15.34% of cobalt (Figure 4.22) and the concentration is inversely proportional to the plating current density. Majid R. Kalantany [90] reported the corrosion property of the zinc cobalt co-deposit and the dependency of the property on the concentration of cobalt in the deposit. The concentrations reported varies widely ranging from 0.35% to 19.9% cobalt and concluded that the coating with a cobalt concentration in between 4.6 to 10.5% showed no reduction in corrosion rate and the coating becomes more noble to the substrate.

The open circuit potential measured for the zinc cobalt deposits under air-agitated condition at various plating current densities are given in table 4.5.
Table 4.5 showing the open circuit potential obtained at various plating current density for the deposit obtained under air-agitated condition.

<table>
<thead>
<tr>
<th>Plating current density</th>
<th>Open circuit potential (Vs Ag/Agcl) mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-915</td>
</tr>
<tr>
<td>2</td>
<td>-931</td>
</tr>
<tr>
<td>3</td>
<td>-836</td>
</tr>
<tr>
<td>4</td>
<td>-870</td>
</tr>
<tr>
<td>5</td>
<td>-675</td>
</tr>
</tbody>
</table>

Figure 4.57 Measured open circuit potential versus cobalt concentration after 1 hour for the coating obtained under air-agitated condition.
Chapter IV Electrodeposition of Zinc-Cobalt Alloy

Figure 4.57 shows the plot for the measured open circuit potential in relation to the concentration of cobalt in the deposit. Thus the coating obtained at $2A/dm^2$ with a cobalt concentration of 10.93% has given the less noble value indicating high degree of protection when compared with the potentials registered by the other coatings. Short et al. [36,37] demonstrated that the coating with cobalt content of 11-14% cobalt in the deposit offers the maximum protection. Thus in this case the deposit at $2A/dm^2$ is less noble compared to the other deposits obtained at other current densities. As seen in the Figure 4.57 the general trend is an increase in the less noble nature of the deposit with increase in cobalt content. The AFM scans for these deposit shows crystalline of more uniform deposits up to $3A/dm^2$. Based on the atomic radius it can be assumed that the smaller clusters seen around the bigger clusters could be the cobalt atoms. This is also supported by the fact that these deposits show more noble potential compared to the deposits obtained at lower plating current densities. Also at high current density the coating is more discontinuous and hence the exposed area of mild steel increases with increased in plating current density resulting in low performance.

Figure 4.58 shows the measured open circuit potential for the zinc-cobalt deposits obtained under sonicated condition and at various plating current densities. The zinc cobalt deposits obtained at plating current densities 1,2 and $3A/dm^2$ show less noble potential (more protection)
compared to the other two plating current densities. At plating current
densities 4 and 5 A/dm² the coating is more noble to the substrate
resulting in failure of the coating to protect the substrate from corrosion.

![Graph showing potential vs cobalt concentration](image)

Figure 4.58 Measured open circuit potential versus plating
current density of the deposits obtained under sonicated condition

The plot of cobalt concentration versus open circuit potential after
1 hr immersion shows that the coatings with high cobalt content were
more noble to the substrate. Since the coating with high cobalt content
lack any particular crystal geometry it is hard to predict the relation
between any possible phase separation and failure to protect the
substrate. Figure 4.59 shows the comparison between the open circuit
potential of the zinc cobalt deposits obtained under both air-agitated and
sonicated conditions. From the figure it is clear that the zinc cobalt
deposits obtained under sonicated conditions were less noble compared
to the deposits obtained under air-agitated condition. This trend continues up to $3 \, \text{A/dm}^2$ beyond which (at 4 and $5 \, \text{A/dm}^2$) zinc cobalt deposit obtained under air-agitated condition becomes less noble compared to the sonicated batches. At these plating current densities the zinc-cobalt deposit obtained under sonicated condition failed to protect the substrate.

![Graph showing comparison of open circuit potential after 1 hour of deposits obtained under sonicated and air-agitated conditions](image)

**Figure 4.59** Comparison of open circuit potential after 1 hour of deposits obtained under sonicated and air-agitated conditions

Figure 4.60 shows the cobalt concentration versus potential measured for both sonicated and air-agitated conditions. As discussed earlier. The deposit obtained under sonicated condition is less noble compared to the air-agitated deposits. It should be noted that the variation of cobalt concentration is very narrow over the entire range of
plating current density for the deposits obtained under sonicated condition and the coating is less noble compared to the deposits obtained under air-agitated condition. Figures 4.58 and 4.59 shows the open circuit potential over a period of 80 hours for the sonicated and air-agitated deposits.

![Graph showing open circuit potential comparison](image)

Figure 4.60 Comparison of open circuit potential of deposits obtained under sonicated and air-agitated condition in relation to their respective cobalt concentration in the deposit.