Executive summary

Corrosion resistance of Zn-Co-Fe alloy coatings on high strength steel

Problem area

Cadmium has been used for decades as corrosion protective layer on steel. It provides good barrier and sacrificial protection and additionally has a corrosion potential close to that of aluminium, therewith preventing accelerated corrosion of aluminium in a galvanic couple with cadmium-coated steel. However, legislation makes the use of cadmium more and more expensive, thereby forcing the industry to search for alternatives.

Zinc is being used extensively as corrosion protective coating on steel, as well. Its sacrificial properties are very good and additional barrier protection is achieved by painting. Due to the large difference in corrosion potential between steel and zinc the zinc coatings do not last long once the paint has been damaged. Alloying of the zinc with more noble elements like iron, cobalt and nickel is recognised as a method to decrease the difference in corrosion potential between the protective coating and the steel substrate and thereby increase the coating life once the paint is damaged.

Most researchers investigated zinc-alloy coatings with low concentration of alloying elements. During the present investigation the concentration is optimised to decrease the dissolution rate in case of paint damage.

Description of work

Zinc-alloy coatings containing up to 40 wt% of cobalt and up to 1 wt% of iron are deposited onto high strength steel substrates and their corrosion protection capabilities are evaluated using electrochemical techniques and accelerated corrosion experiments.

Results and conclusions

Increasing the Co content moves the open circuit potential towards less negative values, reaching that of cadmium above 30 wt% Co. Coatings containing >30 wt% Co + 1 wt% Fe are nano-crystalline and show superior corrosion resistance as compared to coatings with lower Co content. Upon longer immersion the alloy layer becomes more noble due to de-zincification, but simultaneously the corrosion current density decreases. The corrosion resistance determined with the electrochemical techniques was confirmed by accelerated corrosion test, which shows superior corrosion resistance for cadmium and zinc-alloy coatings with a high Co content.

Applicability

The high cobalt-content zinc-alloy coatings have promising properties for replacing cadmium as corrosion protective layer on high strength steels.

Before these coatings can be applied on aircraft other properties relevant for aerospace applications should be tested successfully, such as paint adhesion, corrosion protection capabilities when painted and strip ability.

Corrosion resistance of Zn-Co-Fe alloy coatings on high strength steel

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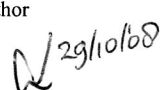[3] TNO

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Abstract

The corrosion properties of electrodeposited zinc-cobalt-iron (Zn-Co-Fe) alloys (up to 40 wt-%
Co and 1 wt-% Fe) on steel were studied by using various electrochemical techniques and
compared with zinc (Zn) and cadmium (Cd) coatings in 3.5 % NaCl solution. It was found that
with an increase in Co content in the coating the open circuit potential (OCP) became more
positive than that of the zinc coating. For Co contents higher than 30 wt-% the OCP shifted
close to that of Cd, but still remained electronegative to the steel substrate. Zn-Co-Fe coatings
with ≥ 30 wt-% Co +1 wt-% Fe are nano-crystalline in nature and show superior corrosion
resistance as compared to the Zn, low Co content Zn-Co-Fe and Cd coatings. During longer
immersion, Zn-Co-Fe alloys with 34-40 wt-% Co became more noble to steel due to
dezincification of the surface but the corresponding corrosion current density decreased. The
corrosion resistance determined by the electrochemical techniques are confirmed by salt spray
testing showing the superior corrosion resistance for Cd and high Co content Zn-Co-Fe alloys
and poor performance of alloys with lower Co contents and pure Zn.

Contents

1 Introduction

Corrosion protective coatings form artificial intermediate layers between the corrosive environment and the underlying metal substrate. In general, the coatings can protect the metal substrates by two main mechanisms: sacrificial and barrier protection mechanisms. Cadmium (Cd) has been used extensively as a barrier and sacrificial coating for steel applications in aerospace, automobile, electrical and fasteners industries because of its excellent corrosion resistance and mechanical engineering properties [1,2,3]. However, Cd is banned due to its toxic nature and stringent environmental regulations [4]. Hence, due to restrictions on Cd, alternate coatings to Cd are being actively explored [2,5,6]. The application of a zinc (Zn) coating is recognized to provide excellent protection to steel against corrosion mainly because of its sacrificial behaviour, by virtue of its low standard electrode potential (E_0 = -1.07V vs. SCE. It is reported [2,7] that the difference in the potential of the coating and the substrate acts as a driving force for the corrosion of the sacrificial coating and protection of steel under corroding conditions. Because of the relatively large difference in electronegativities of Zn and (AISI-4340) steel (E_0= -0.65V vs. SCE), rapid dissolution of Zn occurs under corroding conditions and reduces the coating life of pure Zn on steel, provided the coating is damaged. This problem of rapid dissolution has been mitigated by alloying Zn with cobalt (Co) and iron (Fe) that will bring the E_0 closer to the steel substrate and herewith reduces the driving force for dissolution and enhance the corrosion resistance for a longer period of time. However, most of the researchers and industries emphasize on using Zn-Co and Zn-Fe alloys with lower amount of Co and Fe in the alloys [8,9]. At present, the optimum content of Co and Fe in the coating and their protection mechanism are still matters of controversy. These Zn-Co and Zn-Fe alloy coatings are anomalous in nature (i.e. the less noble element Zn deposits preferentially) and work well in combination with chromate passivation [10]. However, these coatings, with low alloying element contents, possess E_0 near pure Zn and the potential difference remains large: therefore the coating is still prone to rapid dissolution. Besides, due to the restrictions on the use of chromates in the near future and having relatively less corrosion resistant properties in the unpassivated state, these coatings cannot be considered as true replacements for Cd. There is little information available in literature on Zn-Co and Zn-Co-Fe electrodeposition with Co contents higher than 10 wt-% and their corrosion resistance, perhaps due to the anomalism associated with these coatings [11-13].

The present research focuses on the study of the corrosion resistance of electrodeposited Zn-Co-Fe alloy coatings (with a range of Co contents), also in comparison with Cd and Zn coatings. Corrosion resistant properties of these coatings are measured by the use of Open Circuit Potential (OCP), Anodic and Cathodic Potentiodynamic Polarization (APP / CPP) and Linear Polarization Resistance (LPR) measurements. In addition, salt spray tests were performed to

compare the corrosion protection of high alloy Zn-Co to commercial Cd and low alloy Zn-Co-Fe coatings.

2 Experimental

2.1 Electrodeposition of Cd, Zn and Zn-Co-Fe alloys

2.1.1   Base material and general procedure

The Cd, Zn and Zn-Co-Fe alloy coatings for electrochemical testing and neutral salt spray testing were electrodeposited onto both sides of test pieces made of AISI 4340 steel. The typical composition of the AISI 4340 steel is presented in table 1. Before deposition the samples were thoroughly cleaned: chemical and electrolytic (alkaline) degreasing followed by pickling and activation of the surface in an acid medium (8 vol.% HCl). After these preparation steps, the samples were immediately put in the electrolyte to prevent the formation of an oxide layer on the surface. After plating, the samples were thoroughly washed with de-mineralized water and ethanol, then dried with hot air and weighed.

Table 1   Composition of AISI 4340 high strength steel base material

Element	C	Mo	Mn	Ni	Cr	Si
Wt-%	0.4	0.25	0.73	1.74	0.8	0.25

2.1.2   Cd Coating

Cd was electrodeposited under galvanostatic conditions at a current density of 3.5 A/dm^2 from a cyanide bath. The bath temperature was maintained at 25 °C and the electrodeposition was done without bath agitation for ~7 minutes in order to get a coating thickness of ~10 μm. An overview of the electrolyte composition and plating parameters are presented in table 2.

Table 2   Electrolyte formulation and process parameter settings for electrodeposition of a Cd coating on high strength steel

Electrolyte composition	Conditions of deposition
110g/l NaCN	**pH:** 13.0 ± 0.2
32 g/l CdO	**Temperature:** 25 °C
15-60 g/l Na$_2$CO$_3$	**Current Density:** 3.5 A/dm^2
2-3 min. rinsing in flowing cold water and hot air dry	

2.1.3   Zn and Zn alloy coatings

The Zn and Zn-Co-Fe alloy coatings studied by electrochemical techniques were electrodeposited from chloride salts. A detailed overview of the composition of the electrolytes and plating parameters is presented in table 3. The electrolytes for both Zn and Zn-Co-Fe electrodeposition were acidic at a pH in the range of 3.5 ± 0.2. The electrodeposition was carried out at a temperature of 35 °C at 2.0 A/dm- for various durations of time in order to electrodeposit a range of compositions. The parameters were adjusted to obtain a coating layer of ~10 μm thickness.

The deposits were analyzed by Scanning Electron Microscopy (SEM). The composition of the coatings was determined by using Energy Dispersive X-ray (EDX) analysis at 20-30 kV, as shown in table 4.

Table 3   Electrolyte formulation and process parameter settings for electrodeposition of Zn and Zn-Co-Fe coatings on high strength steel

Electrolyte composition	Conditions of deposition
136 g/l (1.0M) $ZnCl_2$	**pH:** 3.5 ± 0.2
23.8-238 g/l (0.1-1.0M) $CoCl_2 \cdot 6H_2O$ [*]	**Temperature:** 35 °C
6.3 g/l (0.05M) $FeCl_2$	**Current Density:** 2.0 A/dm^2
180g/l (2.5M) KCl	
20g/l (0.4M) $(NH_4)_2Cl$	
25g/l (0.5M) H_3BO_3	

* Zinc deposition is carried out from the same electrolyte without the addition of $CoCl_2$

Table 4   Coating specimen codes and typical compositions of Zn-Co-Fe alloys

Coating specimen code	Element content (wt-%)
Zn-Co-Fe-1	0.7 % Co +0.3 % Fe
Zn-Co-Fe-2	1.5 % Co+0.3% Fe
Zn-Co-Fe-3	2.5 % Co +0.5 % Fe
Zn-Co-Fe-4	3.5 % Co +0.5 % Fe
Zn-Co-Fe-5	5.5 % Co +0.5 % Fe
Zn-Co-Fe-6	18 % Co +1 % Fe[*]
Zn-Co-Fe-7	32 % Co +1 % Fe[*]
Zn-Co-Fe-8	35 % Co +1 % Fe[*]
Zn-Co-Fe-9	40 % Co +1 % Fe[*]

* ± 0.2 wt-% Fe

For the intermittent salt spray test high alloy Zn-Co, low alloy Zn-Co-Fe and Cd coatings of 10 μm thickness were electrodeposited on two types of high strength steel, i.e. 300M and AerMet 100, panels. Before coating deposition the steel panels were hot alkaline degreased, anodic alkaline degreased and pickled in 8 % HCl. In order to obtain sufficient adhesion on the high strength steels a sulphuric acid based nickel-strike was applied before depositing the

coatings. After deposition the coatings were passivated and hydrogen embrittlement relieved by heat-treatment at 190 °C for 24 hours.

The high alloy Zn-Co, 30 wt-% Co, coating was deposited from the bath given in table 3 with 1.0 M $CoCl_2 \cdot 6H_2O$, but without Fe addition. Cd coatings were deposited industrially and in the laboratory from the bath given in table 2. The low alloy Zn-Co-Fe, 1 wt% Co and 1 wt% Fe, coatings were deposited using the commercial noncyanide Zincrolyte®NCZ-191 process (Cookson Electronics). These coatings were prepared both on laboratory scale and on industrial scale at a job coater. The Cd and low-alloy Zn-Co-Fe were passivated with a chromate conversion coatings (CCC) in a solution of 200 g/l $Na_2Cr_2O_7.H_2O$ and 10 ml/l H_2SO_4 at pH 1 and room temperature for 20 seconds. The passivated coatings were dried at 70 °C for 1 hour. The high alloy Zn-Co alloy could not be passivated using this process. Additionally high alloy Zn-Co and low-alloy Zn-Co-Fe were passivated by a trivalent chrome based conversion coating (TCC) as a less hazardous and environmentally more benign alternative to the hexavalent chrome based CCC. The thick yellow TCC was applied using the commercial Permapass® 3095 process (Cookson Electronics) at pH 1.8 and 60 °C for 60 s. The passivated coatings were dried at 100 °C for 1 hour.

2.2 Corrosion Studies by Electrochemical Techniques

Three types of electrochemical measurements were used to determine the corrosion protection properties of the above-mentioned metal coatings on steel: Open Circuit Potential (OCP, for 1 hour and 120 hours), Anodic and Cathodic Potentiodynamic Polarization (APP/CPP) and Linear Polarization Resistance (LPR) measurements. The measurements were performed in an Avesta cell containing a platinum counter electrode and Saturated Calomel Electrode (SCE) as a reference electrode. All potential values in this paper are referred to SCE, unless mentioned else.

For the OCP measurements the samples were immersed in neutral 0.6 M NaCl solutions for 1 hour and 120 hours under free corroding conditions and the open circuit potential was recorded. The solution was neither de-aerated nor agitated during the measurement time and was kept at a constant temperature of 25 °C.

For the APP measurements, the samples were immersed in quiescent 0.6 M NaCl solutions for 1 hour to establish a relatively constant OCP value. Then the anodic polarization measurements were recorded starting at -0.13 V vs. OCP and ending at +0.5 V vs. OCP. The scan rate was 0.50 mV/sec and solutions were neither de-aerated nor agitated during tests. From the polarization curves, the corrosion current density and the corrosion potential were measured and verified by using both Tafel and Butler-Volmer equation fitting with CorrView Software.

In case of the CPP measurements, after 1 hour immersion in 0.6 M NaCl solution for stabilizing the OCP value, the system was polarized cathodically from the OCP value to -1.8 V vs. SCE.

With LPR measurements, the polarization resistance of a material is defined as the slope of the potential-current density ($\Delta E/\Delta I$) curve at the free corrosion potential, yielding the polarization resistance R_p that can be related (for reactions under activation control) to the corrosion current by the Stern-Geary equation, as presented in Equation 1:

$$R_p = \frac{B}{I_{corr}} = \frac{(\Delta E)}{(\Delta I)} \Delta E \to 0 \qquad (1)$$

In which: Rp is the polarization resistance , Icorr the corrosion current, B is the proportionality constant, which can be calculated according to Equation 2 from b_a and b_c, the slopes of the anodic and cathodic Tafel slopes respectively.

$$B = \frac{b_a \times b_c}{2.3(b_a + b_c)} \qquad (2)$$

During LPR the potential was swept linearly from –15 mV to +15 mV vs. OCP at a scan rate of 0.17 mV/sec. The scan was repeated 30 times and before starting the scan the OCP of each coating was measured for 1 hour. This allows the changes in the corrosion resistance of the coatings to be observed throughout the immersion. The appropriate values of b_a and b_c were obtained from the sweeps and were used in the calculation of the polarization resistance.

2.3 Salt Spray testing

Neutral salt spray tests were conducted on coated samples in accordance with ASTM B117. The time taken to 5 % red rust on the panel surface was used to assess the corrosion performance of the coating. The time recorded may only help in making a comparison of various coating performances. A MASTMAASIS (Modified ASTM Acetic Acid Salt Intermittent Spray) test was conducted according to ASTM G85-Annex 2. The test was run for 1000 hours and the time to the first occurrence of red rust was used to asses the corrosion protection offered by the coatings.

3 Results

3.1 Sacrificial Properties of Coatings

The corrosion resistance of Cd, Zn and a range of Zn-Co-Fe alloy coatings with a variation of Co (0.7-40 wt%) and Fe (0.3-1.0 wt%) in the deposits are studied and compared. The specimen codes and compositions of all Zn-Co-Fe alloy coatings, measured by EDX, are presented in table 4.

The sacrificial properties of metal coatings are investigated by the measurement of the OCP with time. The OCP measurement results obtained in quiescent 0.6 M NaCl solutions are shown in figures 1 and 2 for 1 hour of immersion and in figure 3 for 120 hours of immersion.
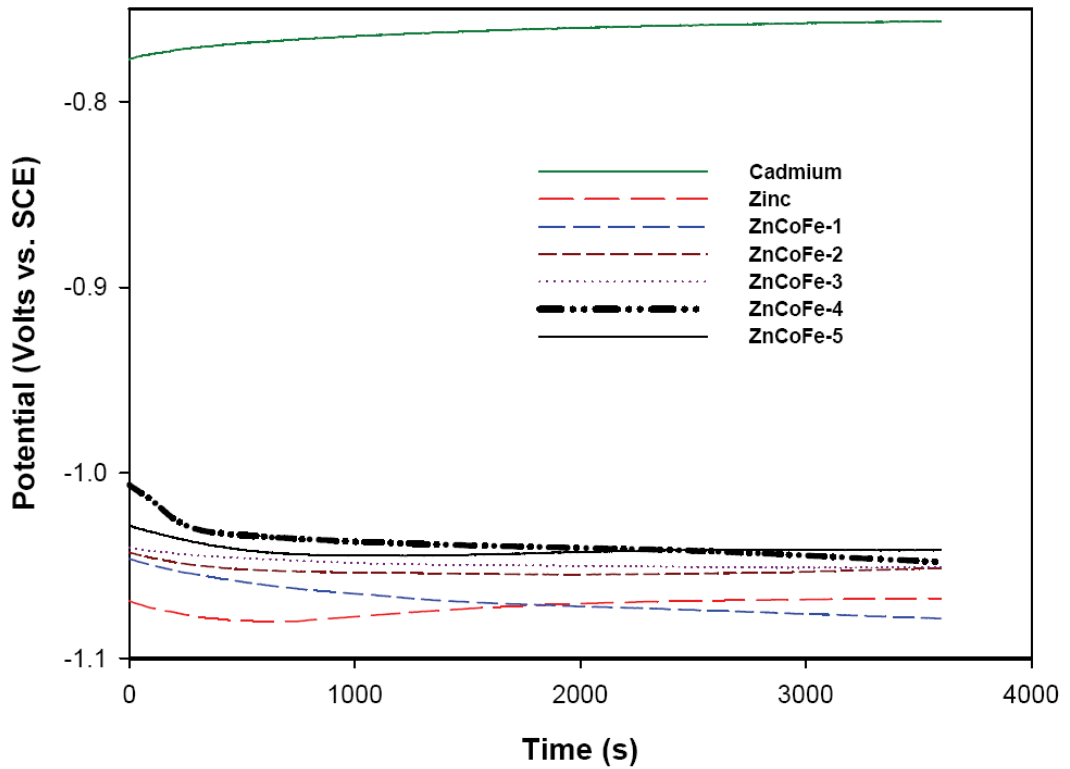
Fig. 1   *OCP curves of Cd, Zn and Zn-Co-Fe coatings 1 to 5 during 1 hour immersion in 0.6 M NaCl solution at room temperature*
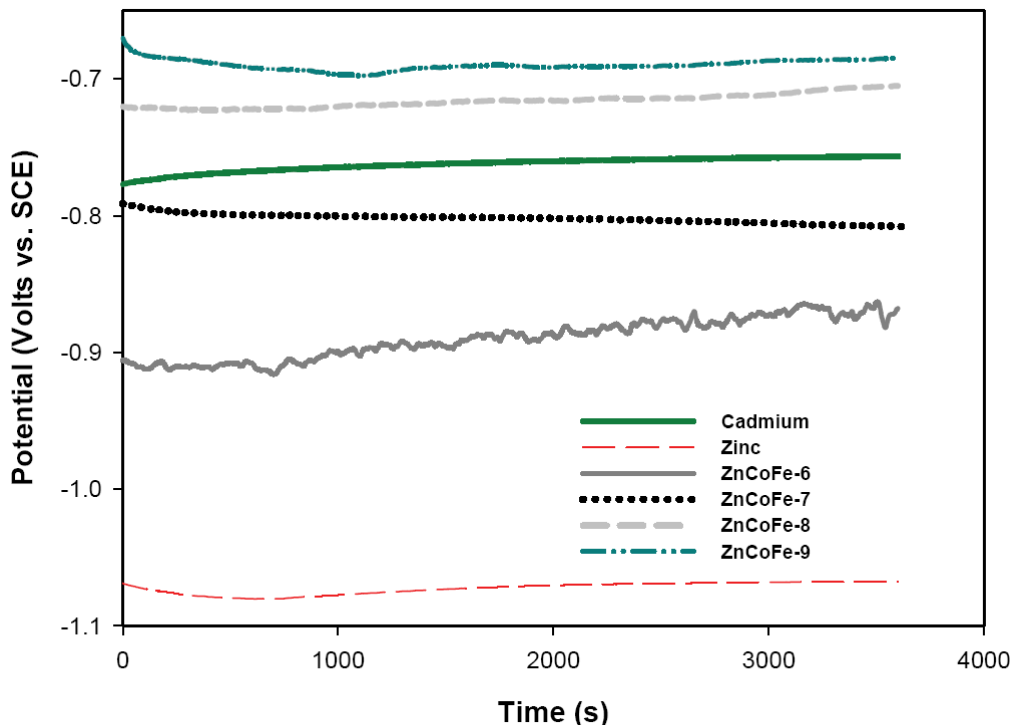

Fig. 2   *OCP curves of Cd, Zn and Zn-Co-Fe coatings 6 to 9 during 1 hour immersion in 0.6 M NaCl solution at room temperature*

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An OCP value of -0.68 V vs. SCE was measured for AISI 4340 steel in 0.6 M NaCl solutions. Figure 1 shows a comparison between Zn, Zn-Co-Fe alloy coatings 1 to 5 (with relatively low Co content between 1-7 wt%) and a Cd coating. It is evident from figure 1 that the OCP curves for Zn-Co-Fe alloys 1 to 5 are very close to that of the pure Zn. A large potential difference between these low Co content Zn-Co-Fe coatings and the steel substrate exists.

In contrast to figure 1, the OCP curves for Zn-Co-Fe alloys 6 to 9 (with relatively high Co content between 18-38 wt%), shown in figure 2, are closer to that of Cd. The potential difference between these Zn-Co-Fe alloys and steel is smaller compared to that between Zn and steel. With further increase of the Co content (> 40 wt%) in the Zn-Co-Fe alloy the OCP becomes more noble than steel and would not be able to protect the steel sacrificially. In general, it is shown in figures 1 and 2 that as the Co content of the Zn-Co-Fe alloys increases the OCP shifts towards more positive potential until it becomes electropositive to steel.

Figure 3 shows the evolution of the OCP for both low and high Co content Zn-Co-Fe alloys during immersion for 120 hours in 0.6 M NaCl solution. It is shown that the OCP for Zn-Co-Fe-2 and Zn-Co-Fe-4 alloys did not change much compared to that for the 1 hour immersion measurement. In the case of the higher Co content Zn-Co-Fe-7 and Zn-Co-Fe-8 alloys the OCP has shifted to more positive potentials for longer exposure times. In case of Zn-Co-Fe-8 alloy the OCP has even shifted to a more positive value than steel. This indicates that after a long immersion period the high Co-content coatings have become more noble than steel.
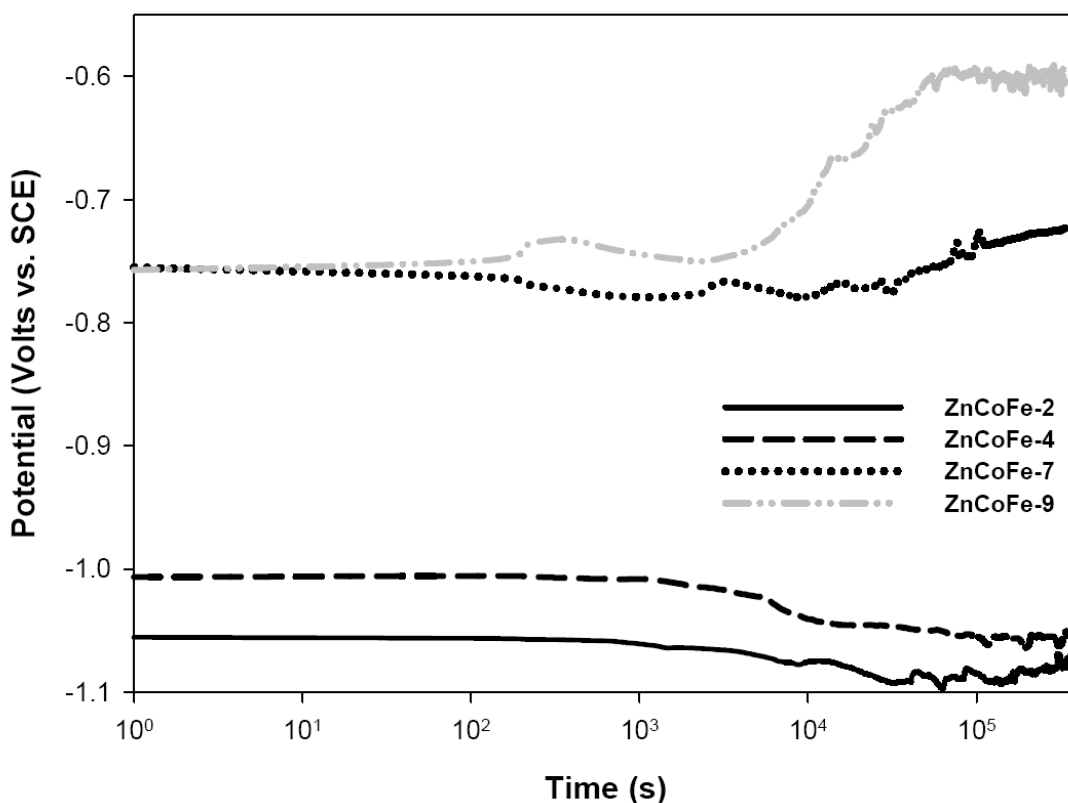

Fig. 3   OCP curves of Zn-Co-Fe coatings 2, 4, 7 and 9 during 120 hours immersion in 0.6 M NaCl solution at room temperature

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3.2 Barrier Properties of Coatings

3.2.1 Anodic Potentiodynamic Polarization (APP) Measurements

APP measurements are used to determine the barrier resistance of the coatings by measuring the corrosion current density. APP sweeps were carried out on all electrodeposited coatings (i.e. Cd, Zn and Zn-Co-Fe alloys) after 1 hour immersion in 0.6 M NaCl solutions and shown in figures 4 and 5. For each coating, a relatively large increase in current density is obtained for a small increase in polarization overpotential, indicating that they are essentially active in this environment. Corrosion current density values, presented in table 5, were determined from the cathodic sweeps using Tafel extrapolation techniques. The curves show that zinc and Zn-Co-Fe 1,4, 5, 6 alloys show higher dissolution rate. While the Cd and Zn-Co-Fe 2, 3, 7, 8 and 9 alloys show a lower corrosion current density and therefore a lower dissolution rate. The corrosion current density for Zn-Co-Fe alloys 7 and 8 is also significantly lower than that for Cd and Zn coatings.
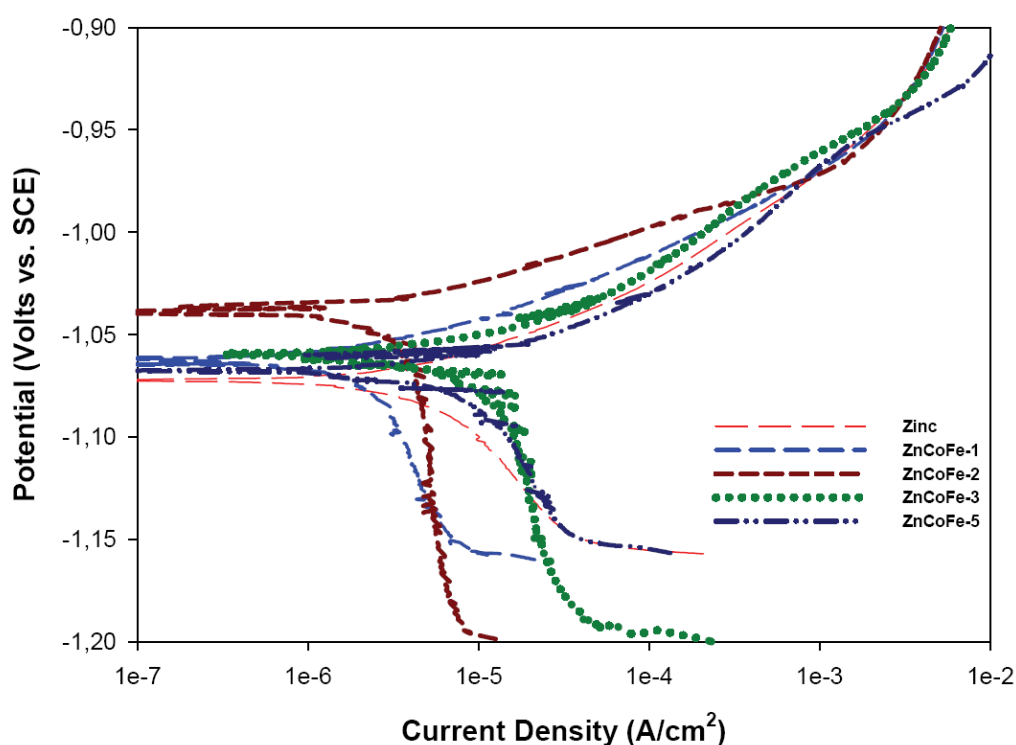

Fig. 4   Polarization curves for Zn and Zn-Co-Fe coatings 1, 2, 3 and 5 after 1 hour immersion in 0.6 M NaCl solution at room temperature
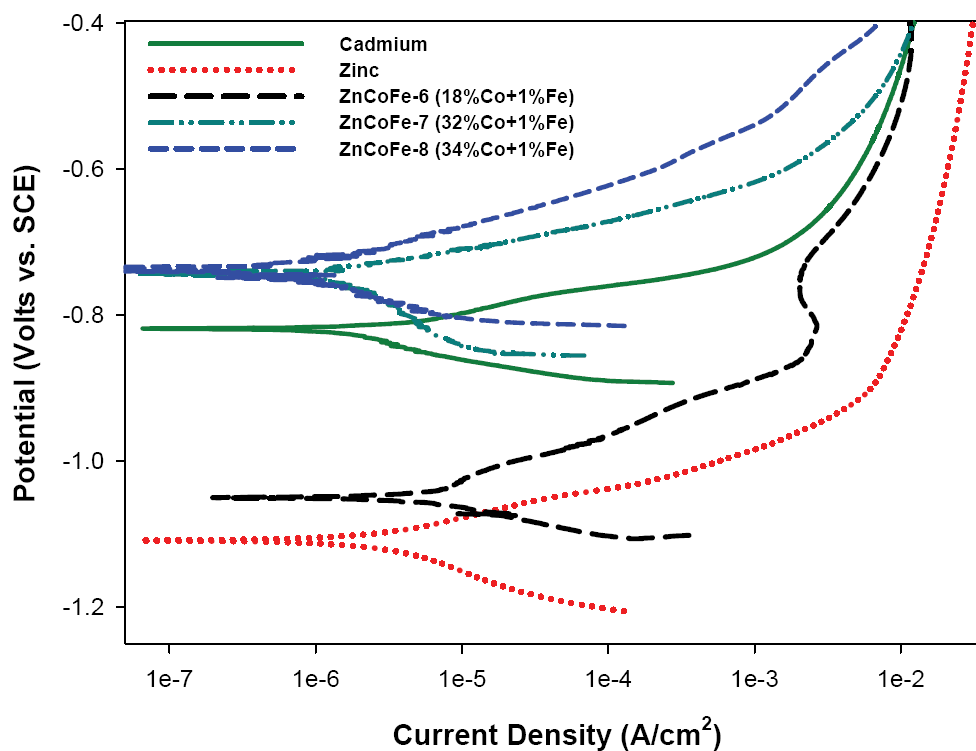
Fig. 5   Polarization curves for Cd, Zn and Zn-Co-Fe coatings 6, 7 and 8 after 1 hour immersion in 0.6 M NaCl solution at room temperature

Table 5   Open circuit potential (OCP) and corrosion current density (i_{corr}) values after 1 hour of immersion in 0.6 M NaCl

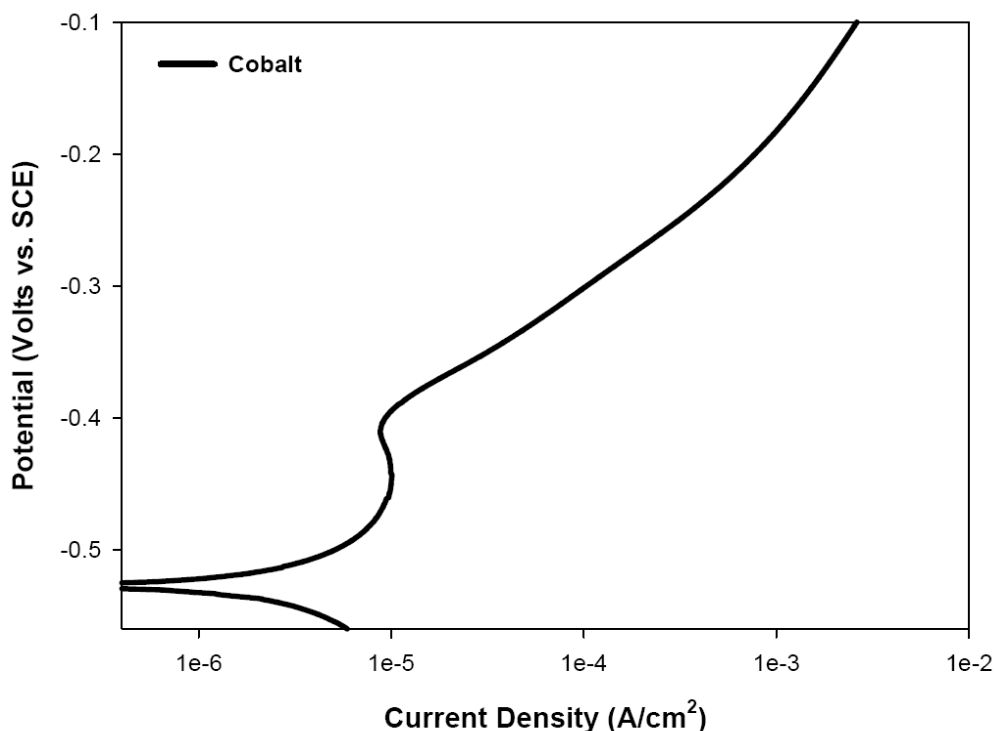| Coating specimen code	OCP (V vs. SCE)	i_{corr} (μA/cm²)
Cadmium	-0.792	2.20
Zinc	-1.071	6.00
Zn-Co-Fe-1	-1.068	8.00
Zn-Co-Fe-2	-1.060	2.30
Zn-Co-Fe-3	-1.054	3.43
Zn-Co-Fe-4	-1.045	12.0
Zn-Co-Fe-5	-1.035	6.20
Zn-Co-Fe-6	-0.806	4.25
Zn-Co-Fe-7	-0.791	0.77
Zn-Co-Fe-8	-0.763	0.40
Zn-Co-Fe-9	-0.713	1.50

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*Fig. 6   Polarization curve for a pure cobalt coating after 1 hour immersion in 0.6 M NaCl
solution at room temperature*

Figure 6 illustrates the anodic polarization behaviour obtained for an electrodeposited pure Co
coating on steel after 1 hour immersion in quiescent 0.6 M NaCl solution. Figure 6 shows a
clear passive corrosion behaviour at relatively small anodic overpotential in contrast to the
anodic behaviour of the Zn-Co-Fe alloys with relatively high cobalt content level (30-40 wt%
Co).

Figure 7 shows the potentiodynamic polarization curves for Zn-Co-Fe-2, 4, 7 and 9 alloys with
extended immersion times of 120 hours in 0.6 M NaCl solutions. Comparison of the anodic
polarization curves for Zn-Co-Fe-2 and 4 alloys after 1 and 120 hours indicates that the curves
do not change after immersion for 120 hours in the electrolyte and the corrosion current density
remains relatively high, as presented in table 6. The Zn-Co-Fe-7 and 9 alloys (with 32 and 40
wt% Co respectively) show a further decrease in corrosion current density after 120 hours
immersion compared to that after 1 hour of immersion only.

Table 6   Open circuit potential (OCP) and corrosion current density (i_{corr}) values after 120 hours of immersion in 0.6 M NaCl

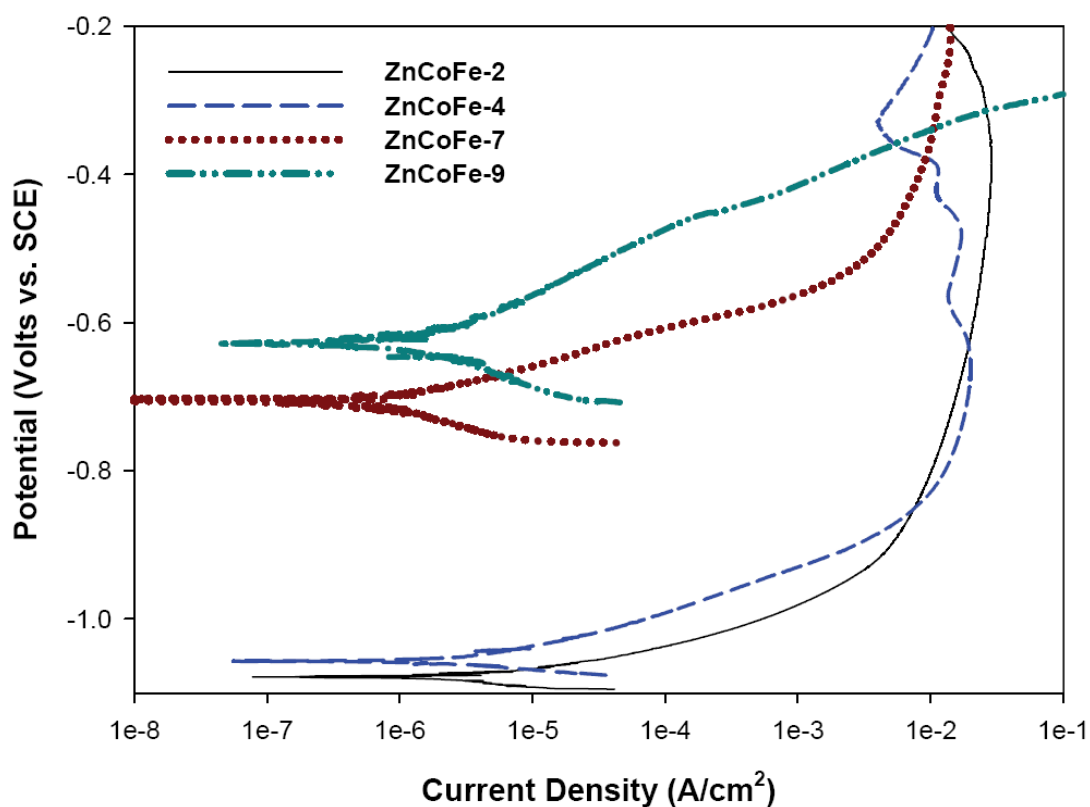| Coating specimen code	OCP (V vs. SCE) after 120 hours	i_{corr} (μA/cm²)
Zn-Co-Fe-2	-1.08	4.07
Zn-Co-Fe-4	-1.04	3.9
Zn-Co-Fe-7	-0.72	0.09
Zn-Co-Fe-9	-0.64	1.06

Fig. 7   Polarization curves for Zn-Co-Fe coatings 2, 4, 7 and 9 after 120 hours immersion in 0.6 M NaCl solution at room temperature
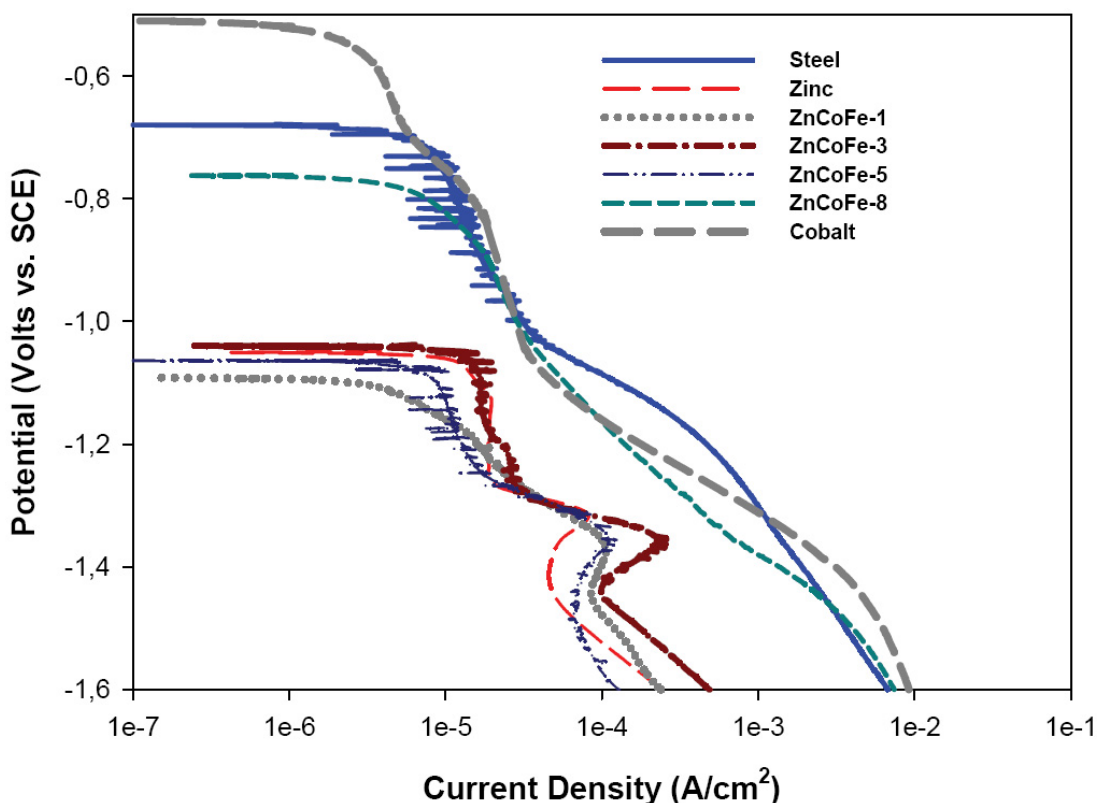
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Fig. 8   Cathodic polarization curves for steel, Co, Zn and Zn-Co-Fe coatings 1, 3, 5 and 8 obtained during immersion in 0.6 M NaCl solution at room temperature

3.2.2   Cathodic Potentiodynamic Polarization (CPP) Measurements

The cathodic polarization curves obtained for Cd, Zn and Zn-Co-Fe alloys are shown in figure 8. The cathodic polarization curve for steel substrate is also shown in figure 8 for comparison. The curves for Zn and Zn-Co-Fe alloys with relatively low Co contents (i.e. 1, 4, 5 wt% Co) show similar cathodic behaviour. These curves show a complex reduction behaviour at -1.3 V vs. SCE, also reported by other researchers [14]. The curves for the Zn-Co-Fe alloys with 40 wt% Co show a cathodic polarization behaviour that is similar to pure cobalt and steel.

3.2.3   Linear Polarization resistance (LPR) Measurements

LPR studies are carried out on pure Cd, pure Zn and Zn-Co-Fe alloys. The resulting graphs of overpotential vs. current density for Cd, Zn and Zn-Co-Fe-1, 4 and 7 alloys after 11 hours of immersion in 0.6 M NaCl solutions are shown in figure 9. The slopes of these lines yield the value of the polarization resistance (R_P). This overpotential vs. current density plot suggests that Cd and Zn-Co-Fe-7 alloy have a rather steep slope indicating very good barrier properties. The less steep slope in case of the Zn-Co-Fe-1 and Zn-Co-Fe-4 alloys indicates a poor barrier resistance against dissolution, herewith suggesting a higher corrosion rates for these alloys.
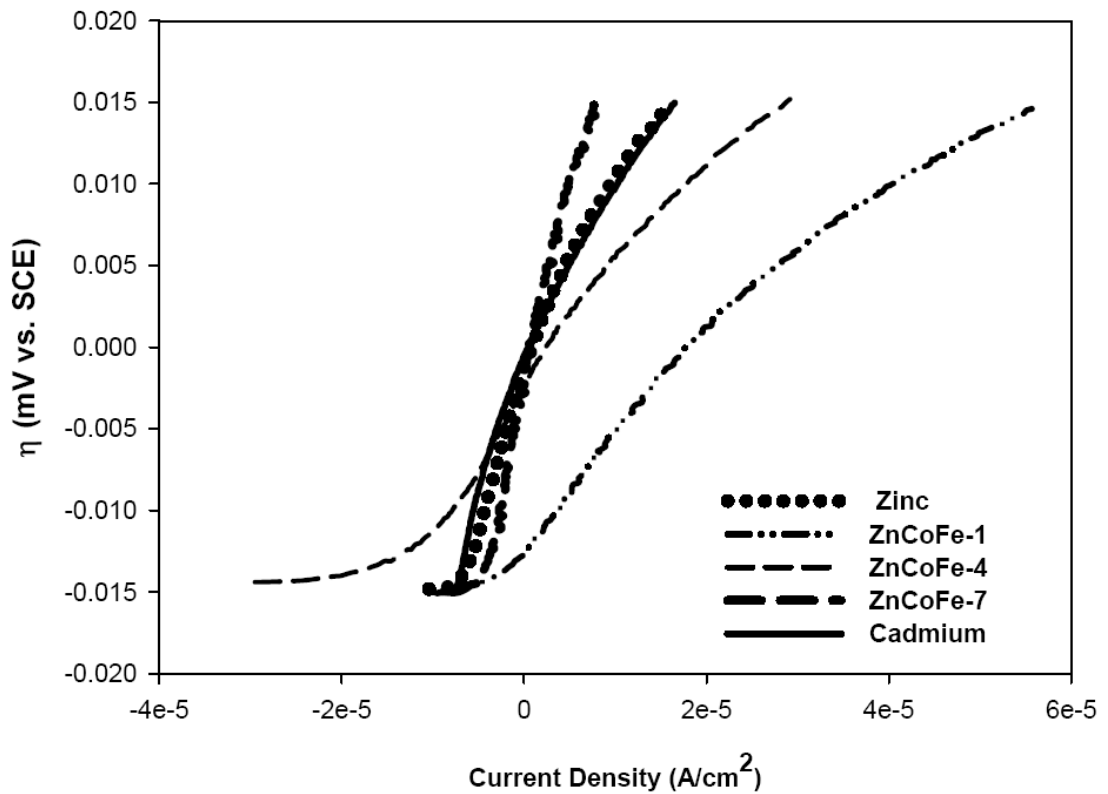
Fig. 9   Linear polarization curves for Cd, Zn and Zn-Co-Fe coatings 1, 4 and 7 after 11 hours immersion in 0.6 M NaCl solution at neutral pH and room temperature
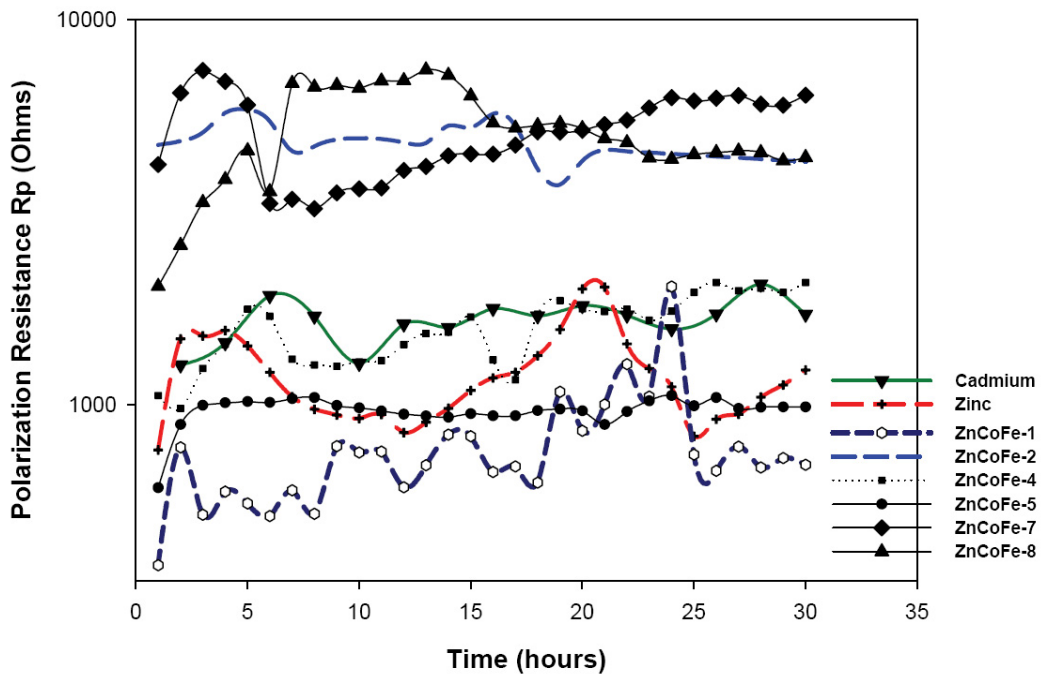

Fig. 10 Plot of polarization resistance versus time for Cd, Zn and Zn-Co-Fe coatings 1, 2, 4, 5, 7 and 8 in 0.6 M NaCl solution at neutral pH and room temperature

Figure 10 shows the plot of polarization resistance values as a function of time for all above-mentioned coatings. It is evident from figure 10 that the polarization resistance is very high for Zn-Co-Fe alloys 2, 7 and 8. The resistance value increases further for Cd and Zn-Co-Fe-7 alloy with time under open circuit conditions. The polarization resistance for Zn-Co-Fe-1, 4 and 5 is lower and does not improve over a longer immersion period. It is noticeable that the resistance increases with increasing Co content with the exception of Zn-Co-Fe-2 alloy which shows excellent barrier properties.

3.3 Salt Spray Testing

The barrier resistance determined by the electrochemical techniques are further investigated by neutral salt spray tests. A comparison of corrosion performance for various coatings is given in figure 11, which confirms the superior corrosion resistance for Cd and Zn-Co-Fe alloys 7, 8 and 9 and poor performance of alloys with lower Co contents and pure Zn.
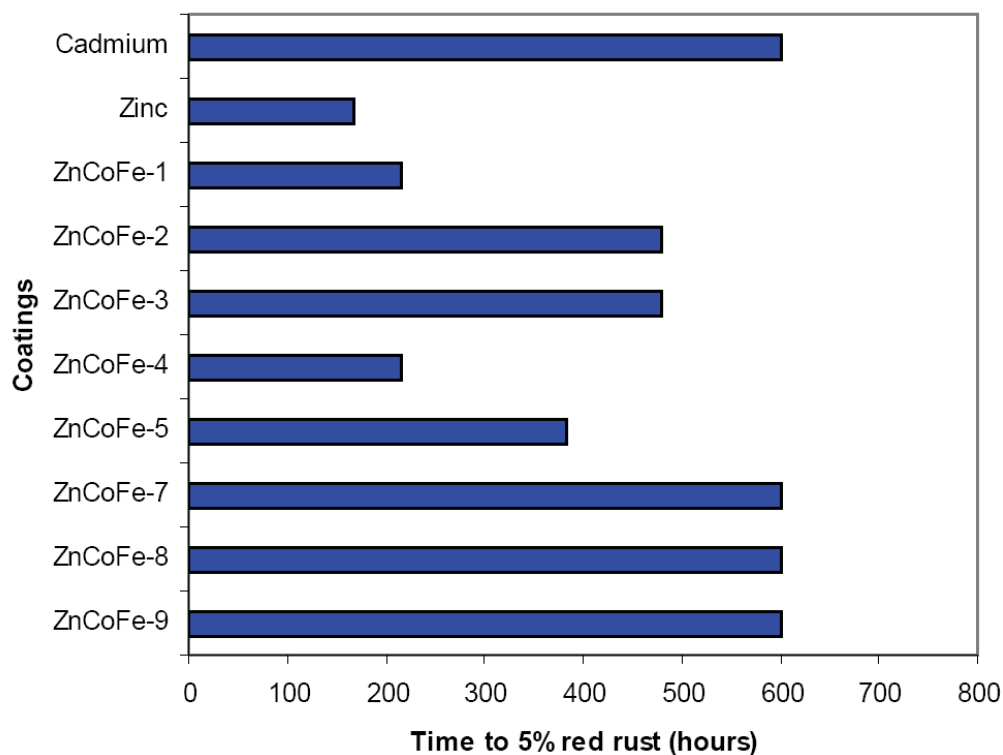
Fig. 11 Comparison of the performance of coated steel sheet exposed to neutral salt fog, according to ASTM B117 (average coating thickness ~10 µm)

The time to the first occurrence of red rust in the MASTMAASIS test is shown in figure 12 for the various coatings. It can be seen that the corrosion resistance of the trivalent chrome (TCC) passivated high alloy zinc coating is equal or better than the other tested coatings on both types of steel. Of the various passivated Cd coatings only the industrial chromate (CCC) passivated

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coating on AerMet 100 gives a similar corrosion protection. Of the various low alloy Zn-Co-Fe coatings only the chromate (CCC) passivated laboratory coatings show an equal time to first red rust occurrence. However it has to be mentioned that the industrial low alloy Zn-Co-Fe coating were considerably thinner, i.e. 6-8 μm compared to 10 μm, than the other coatings. As the coating thickness strongly affects the time to red rust formation it can not be excluded that also trivalent chrome (TCC) passivated low alloy Zn-Co-Fe offers a similar corrosion protection as a trivalent chrome (TCC) passivated high alloy Zn-Co coating.
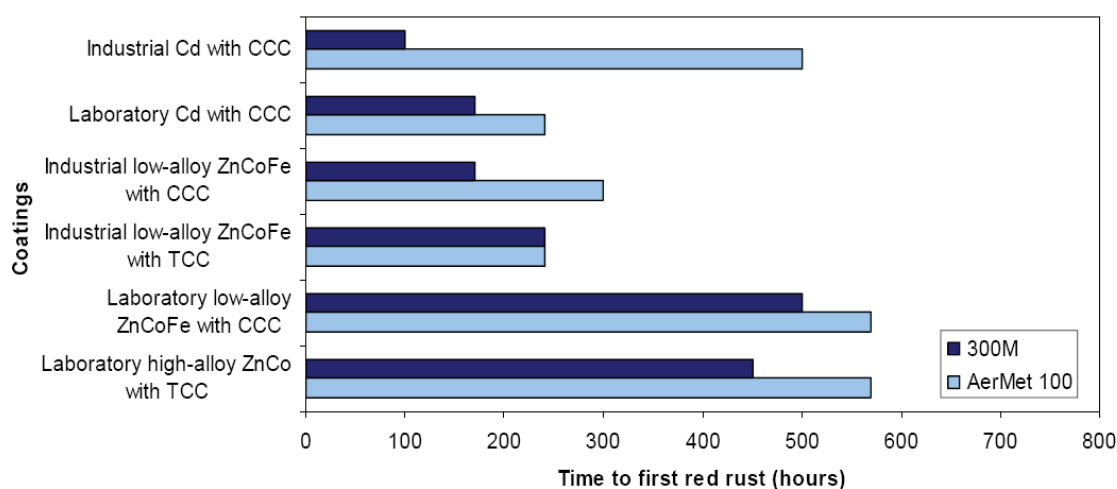

Fig. 12 Time to first occurrence of red rust on high alloy Zn-Co, low alloy Zn-Co-Fe and Cd coatings on 300M and AerMet 100 steel in the MASTMAASIS test

4 Discussion

4.1 Sacrificial Properties

The sacrificial behaviour of various coatings can be predicted with reasonable accuracy by comparing their open circuit potentials with that of the substrate material (AISI 4340 steel) [2,7,15]. Table 5 shows that all coatings of interest are to some extent electronegative to steel (-0.68 V vs. SCE in 0.6 M NaCl) and are expected to provide a certain degree of sacrificial protection to steel.

A large potential difference between the lower Co content Zn-Co-Fe coatings and the steel substrate exists. It can therefore be predicted from the relative potential difference that these coatings are highly sacrificial to steel and, due to a large driving force, prone to rapid dissolution in a corrosive environment, once the base steel substrate is exposed. After 120 hours of immersion in a 0.6 M NaCl electrolyte the OCP value did not increase significantly which can be correlated to the relatively high Zn content and low alloying element concentration.

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The potential difference between the higher Co content Zn-Co-Fe alloys and steel is smaller as compared to that between Zn and steel. Therefore it can be predicted that these Zn-Co-Fe alloy coatings would dissolve less rapidly than the lower Co content Zn-Co-Fe alloy coatings, provided the base steel substrate is exposed, and would protect the exposed steel substrate for a longer period of time. With further increase of the Co content (> 40 wt%) in the Zn-Co-Fe alloy the OCP would become noble to steel and the coating would not be able to protect the steel sacrificially.

It is found that the OCP for Zn-Co-Fe-7 and Zn-Co-Fe-8 alloys shifts to more positive potentials for longer exposure times. In case of Zn-Co-Fe-8 alloy the OCP has even shifted to a more positive value than steel. This indicates that after a long immersion time the coatings have become noble to steel. This potential shift can be correlated to the selective dissolution of Zn from the alloy coating, leaving behind deposits that are rich in Co and causing ennoblement of the surface. This process is also known as the de-zincification mechanism and is reported by other researchers as well [2,16,17]. The ennoblement is a surface phenomenon and results in passivation of the surface. If a coating is scratched then the sacrificial nature of the coating will still be able to play a role.

4.2 Barrier Properties of Coatings

Potentiodynamic polarization and polarization resistance techniques are used to determine the barrier resistance of the coatings by measuring their dissolution rate. In case of pure Co, the anodic polarization curve shows a passive region, which corresponds to a relatively low dissolution rate by the formation of a stable oxide-hydroxide layer in near neutral solutions [18]. The corrosion current density values are calculated using Tafel and Butler-Volmer fits and the values are presented in table 5. It is shown in table 5 that the Zn-Co-Fe-1, 4, 5 and 6 alloys have rather high corrosion current densities. This suggests that they will provide less efficient barrier protection and will dissolve faster under the corrosive conditions investigated. In contrast, Zn-Co-Fe-2, 3, 7, 8, 9 alloys show a significantly lower value of the corrosion current density. The corrosion current densities for Zn-Co-Fe alloys 7 and 8 (in particular) are much lower than that for Zn and Cd, which shows that these coatings will last longer due to a lower dissolution rate in a corrosive environment containing chloride ions. The higher barrier resistance of the Zn-Co-Fe-2, 7, 8 alloys as compared to other coatings is further verified by polarization resistance results, shown in figures 9 and 10.

Table 6 shows that after 120 hours immersion in NaCl electrolyte the corrosion current density values for Zn-Co-Fe-2 and 4 alloys have increased significantly. While for Zn-Co-Fe alloys 7 and 8 the corrosion potential moves to more positive values, but the corrosion current density decreases to a lower value which corresponds to a lower dissolution rate and an increased barrier resistance of these coatings.

It is assumed during the cathodic polarization that from the corrosion potential to -1.25 V vs. SCE the main cathodic reaction responsible for the current density is the oxygen reduction that produces OH⁻ ions, also previously reported by Hinton and Wilson for zinc [14]. The cathodic reduction reaction results in a local increase of pH which is reported to facilitate the formation of $Zn(OH)_2$ on the surface [14,16,18-20]. At -1.35 V, for pure zinc and Zn-Co-Fe alloys 1, 4 and 5, the cathodic current density varies with the potential in a complex manner. The reason for such a behaviour is unknown but also found by other researchers [14]. It suggests that also other reactions, in addition to oxygen reduction, occur simultaneously at the surface.

In case of Cd the excellent corrosion behaviour is due to the formation of a CdO layer on the surface, which prevents further dissolution. In aqueous environment the initial corrosion product layer observed on the surface of zinc coating is $Zn(OH)_2$ which is a good barrier layer and a poor semi-conductor. However, in case of pure zinc and Zn alloys with lower alloying elements the hydroxide layer rapidly de-hydrates to form ZnO, which is voluminous, less adherent and a poor insulator. It is reported by several researchers [16,18-24] that the presence of (iron group metals) Co and Fe at the surface of the alloy contribute to an improved level of protection by increasing the stability of the hydroxide layer, avoiding formation of ZnO, then further forming ZnOHCl which is an insulator. The lower barrier resistance shown by pure Zn and Zn-Co-Fe alloys with lower Co content (alloys 1, 4-6) can be attributed to the formation of a ZnO layer. The excellent barrier resistance of the Zn-Co-Fe7-9 alloys can be attributed to the presence of $Zn(OH)_2$, which is a good barrier layer and a poor semi-conductor. Furthermore, the de-zincification process leaves behind Co at the surface and results in ennoblement of the surface, which also contributes to the barrier resistance as Co itself is a very stable substance in a corrosive medium [2,7,17,21]. In addition, due to local pH rise Co may also further transform to $Co(OH)_2$ which is again very stable [18] and a very good insulator as well.

The presence of one or more phases on a coating surface can also influence the measured corrosion current density values. The higher corrosion current density values for the Zn-Co-Fe-alloys 1, 4, 5 and 6 can be attributed to the presence of more phases of Zn-Co-Fe alloys on the surface as suggested by several peaks in the XRD patterns (shown in Fig. 13) that indicate highly crystalline structures. Some other researchers have also reported the presence of various phases in electrodeposited Zn-Ni alloys (Zn-Ni) with varying Ni contents [19]. As these local microstructural variations adopt different equilibrium potentials in aqueous solutions they are susceptible to local galvanic corrosion. On this basis it is expected that the corrosion rates of the single phase alloys is lower than that of binary or multiphase alloys.

The lower corrosion current densities for the Zn-Co-Fe-alloys 2, 3 and 7-9 are related to the presence of a single phase. For Co contents higher than 30 wt% the Zn-Co-Fe alloys consist of a single phase that contains nano-crystallites (unidentified), as shown by the peak broadening effects of XRD in figure 14.

The corrosion resistance determined by the electrochemical techniques is further verified by salt spray testing which confirm the high corrosion resistance to red rust for Zn-Co-Fe alloys 7, 8 and 9, high alloy Zn-Co and poor performance of alloys with lower Co contents.
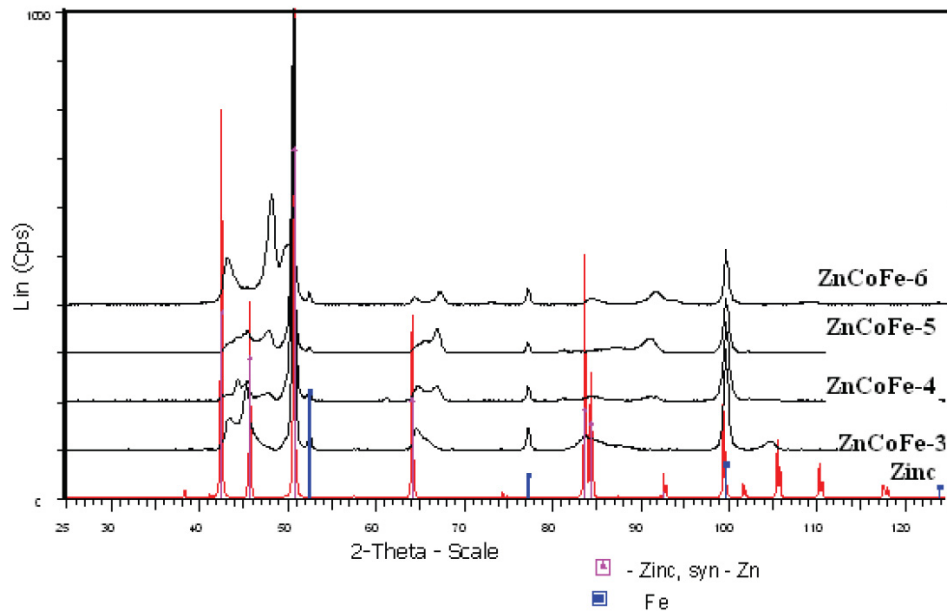

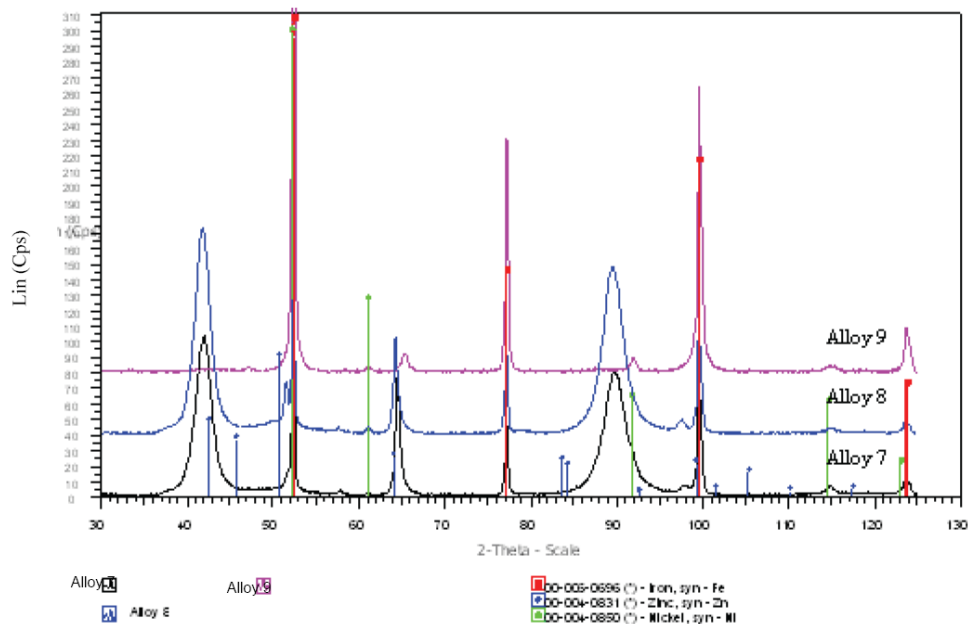Fig. 13 The XRD pattern of Zn-Co-Fe coatings 3,4,5 and 6 determined with CoK-α radiations

Fig. 14 The XRD pattern of Zn-Co-Fe coatings 7, 8 and 9 determined with CoK-α radiations

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5 Conclusions

In the present investigation the corrosion resistance in terms of sacrificial and barrier properties of electrodeposited Zn-Co-Fe alloys (up to 40 wt% Co and 1 wt% Fe) was studied in 0.6 M NaCl solution. The results of the Zn-Co-Fe alloy coatings were also related to those of electrodeposited zinc and cadmium coatings. It is found that Zn-Co-Fe alloys (1-5) with relatively low Co content (< 7 wt%) show OCP values near pure zinc and the potential values do not change significantly for immersion periods up to 120 hours. The large OCP difference between these coatings and steel results in a high driving force for dissolution if the coating is damaged and the underlying steel is exposed. Furthermore, both Zn and Zn-Co-Fe alloys (1 and 3-6) show very poor barrier resistance performance in terms of corrosion current density, as obtained from potentiodynamic polarization measurements, and polarization resistance. The higher corrosion rate is attributed to the presence of binary or multiphase regions present on the surface resulting in local galvanic corrosion. The Zn-Co-Fe-2 alloy shows excellent corrosion resistance properties, which can be attributed to the uniform and single-phase composition of the alloy.

For the Zn-Co-Fe alloys 7 and 8 with relatively high Co content (> 32 wt%) the OCP is shown to be very close to that for a cadmium coating and the OCP difference between steel and the coatings is also lower (like that for cadmium) compared to that of Zn-Co-Fe alloys with relatively low Co content. The Zn-Co-Fe coatings (relatively high Co content) are supposed to protect the steel substrate for a longer period of time. However, due to the de-zincification mechanism, surface ennoblement with Co occurs and the OCP moves to significantly more positive values for longer immersion times. The corrosion current densities are found to decrease during the long immersion measurements.

The corrosion resistance determined by the electrochemical techniques are confirmed by salt spray testing and show the superior corrosion resistance for Cd and high Co content Zn-Co-Fe alloys and poor performance of alloys with lower Co contents and pure Zn.

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