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Dual-Layered Zinc Alloy Coatings for Corrosion Protection

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Abstract

The corrosion behaviour of single and dual-layered zinc-nickel coatings electroplated onto a 2014-T6 aluminium alloy substrate has been investigated using accelerated corrosion testing and electrochemical measurements. Initial studies demonstrated that coatings could be electrodeposited from a nickel sulphate / zinc sulphate bath and that the nickel content could be varied from 3% to 18% by changing the current density. Single layer coatings were prepared having a thickness of 8μm and with various compositions in the range zinc-4% nickel to zinc-17% nickel. Three dual-layer coatings were deposited consisting of a zinc-low nickel layer over-plated with a zinc-high nickel layer. Neutral salt spray testing has shown that the dual-layer coatings are more effective in protecting the aluminium alloy substrate than single layer coatings. Open circuit potential time measurements indicate that there is a loss of zinc from the coatings on exposure to sodium chloride solution. Galvanic corrosion studies made on single and dual-layered coatings coupled to 2014-T6, aluminium alloy demonstrate that the coatings are sacrificial in nature. With the nickel rich coatings, current reversal

occurs after prolonged immersion and the coatings cease to be protective. The dual layered coatings appear to behave in a similar way to the single layer coatings. Galvanic compatibility with structural aluminium–copper alloys may be achieved if coatings with high nickel contents are employed.

Keywords

Corrosion, zinc–nickel plating, cadmium plating, electrical connectors

Introduction

Cadmium plating has been widely used on aluminium alloy electrical connector shells employed on both civil and military aircraft and helicopters. It provides a high level of corrosion protection and ensures galvanic compatibility with structural aluminium alloys. Additionally the electrical resistance between mating components is less than 5 milliohms: well below the specified level.

Previous studies on cadmium replacements for use on steel components and fasteners have identified several potential alternative surface coatings [#ref01][#ref02]. These include aluminium coatings produced either by physical vapour deposition (PVD) or by electro-deposition from an organic bath; electroplated zinc alloy coatings and metallic–ceramic coatings prepared by immersion or spraying techniques. The latter are relatively thick coatings consisting of either zinc or aluminium particles incorporated into a ceramic matrix. The electrical resistance of these coatings is relatively high, making them unsuitable for connector applications.

This study has examined the use of electro-deposited zinc–nickel coatings for connector applications. Previous work [#ref03] has shown that the corrosion behaviour of electroplated zinc–nickel is dependent on the composition. Increasing the nickel content of the deposit, reduces the sacrificial properties of the coating whilst improving the barrier properties. Electrochemical studies indicate that above 15% nickel the coating is no longer sacrificial with respect to 2000 series aluminium alloys, although the corrosion resistance of the coating is high. The use of zinc–nickel coatings for the protection of 2024–T3

sheet aluminium alloys has been described by Alexis et al. [#ref04]. Electrochemical studies found that a 12–14% nickel coating should provide an effective level of protection. However results from earlier studies [#ref05] suggest that this composition will not give good sacrificial protection if the coating becomes damaged. One approach is to deposit a sacrificial coating onto the substrate and then over-plate it with a more corrosion-resistant coating such as zinc-14% nickel. Recent data, published on the corrosion behaviour of layered zinc coatings applied to steel substrates, has demonstrated that in salt fog tests some zinc and zinc-nickel alloy layered structures give better protection to steel substrates than single layer zinc coatings of the same thickness [#ref06]. Methods of producing compositionally-modulated coatings have been reviewed by Leisner et al. [#ref07] and include the dual bath technique and the single bath technique.

In the present research, the corrosion of dual-layered zinc-nickel coatings applied to a 2014-T6 aluminium alloy substrate has been compared with single layer coatings. A method for producing the dual-layer coatings using a single bath technique was employed.

Experimental

Preparation of electroplated test coupons

Test panels, 5cm x 5cm, were cut from 1.8mm thick 2014-T6 aluminium alloy sheet. The nominal composition of the sheet is given as

Cu (3.9 – 5.0%), Mn (0.4–1.2%), Mg (0.2–0.8%), Si (0.5–0.9%), Cr (0.1%)

Prior to electroplating, the surfaces of the aluminium test coupons were first degreased with acetone and allowed to air dry. The samples were then etched in a 10% sodium hydroxide solution followed by a desmut in 50% nitric acid. After desmutting, the coupons were subjected to a zincate immersion pretreatment in order to minimise the formation of oxide prior to electroplating. Details of the treatment times and temperatures are given in Table 1.

Table 1   Pretreatments used for preparation of panels prior to electroplating

Pretreatment	Solution	Immersion time (seconds)	Temperature ^oC
Etch	10% NaOH in de-ionised water	60	50
Desmut	50% nitric acid in de-ionised water	15	20
Zincate	50g dm^{-3} zinc oxide 400g dm^{-3} sodium hydroxide	180	20

Initially, plating trials were conducted using a nickel sulphate / zinc sulphate electrolyte to establish the influence of current density on coating composition. The composition of the bath used is given in Table 2. TRIS was added as a complexant to help stabilise the ageing characteristic of the bath. The surfactant Tween was used to reduce the level of porosity in the resultant film. An antifoaming agent was employed to enable the use of air agitation.

Table 2   Electroplating bath composition and operating conditions

Additive	Concentration
Nickel sulphate	0.75 mol dm^{-3}
Zinc sulphate	0.75 mol dm^{-3}
TRIS – tris (hydroxymethyl) methylamine	0.75 mol dm^{-3}
Tween™	10 cm^3 dm^{-3}
Antifoaming agent	10 cm^3 dm^{-3}

Bath operating conditions	
pH = 6.5	Temperature 20°C

Test coupons were electroplated over a range of current densities from 0.01 A cm^{-2} to 0.3 A cm^{-2} and then examined using a scanning electron microscope fitted with an energy dispersive X-ray analysis facility to allow the coating composition to be determined. Figure 1 shows the variation in nickel content with current density and was used to determine the plating conditions to be employed in the subsequent production of single and dual-layer zinc-nickel coatings.

A series of aluminium alloy coupons were electroplated to produce single layer coatings containing up to 18% nickel. The current density was varied in accordance with Figure 1 to yield coatings with the desired composition. For each current density selected, the plating time was adjusted so that the final coating thickness was 8 μm. Dual-layer coatings were produced by changing the current density part way through the electroplating process. Further details are given in Table 3. In each case the plating time was chosen to produce a layer thickness of 4 μm, giving a total coating thickness of 8 μm.
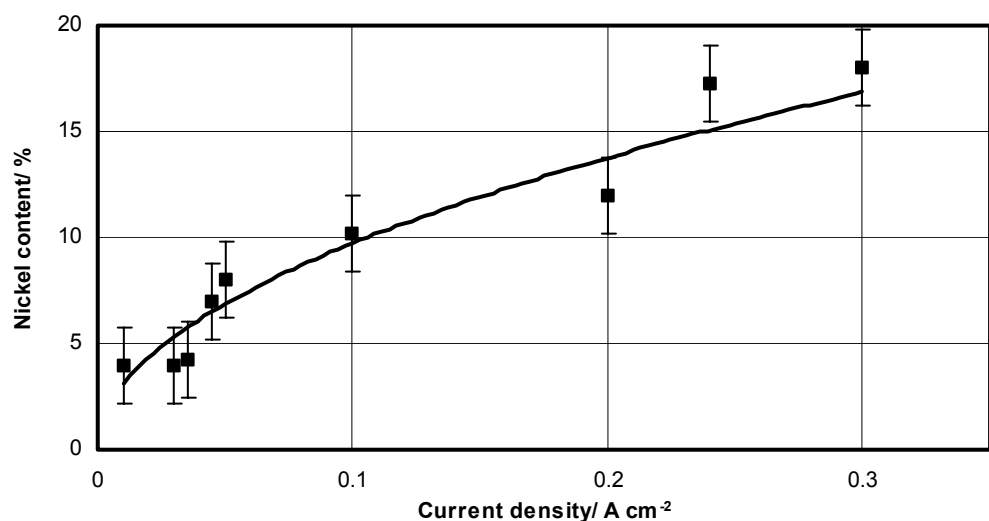
Figure 1   Effect of current density on coating composition

Table 3   Plating conditions used to electrodeposit dual-layer coatings

Applied current density, A cm⁻²		Expected composition, % nickel	
Inner layer	Outer layer	Inner layer	Outer layer
0.02	0.10	5	10
0.02	0.21	5	14
0.10	0.21	10	14

Corrosion studies

The corrosion performance of the electroplated aluminium panels was assessed by exposure to neutral salt fog and by electrochemical measurements.

Exposure to neutral salt fog

Zinc-nickel electroplated panels were exposed to continuous neutral salt fog in accordance with ASTM B117. Exposure times of 2 weeks were employed and following visual inspection, metallographic sections were prepared to allow the depth and extent of corrosion to be determined using optical microscopy.

Total immersion corrosion studies

The variation in open circuit potential with time was monitored for electroplated coupons immersed in 600 mM sodium chloride solution. Test samples, 1.5cm x 1.5cm, were guillotined from the plated panels. Electrical contact was made to the reverse (non-plated) side of the test sample using a bare copper wire, which was attached using a silver loaded epoxy adhesive. The wire was encapsulated in a glass tube and sealed using an epoxy adhesive. The electrode was then coated with a protective lacquer on the non-plated side and on the edges. An area 1cm x 1cm was left unmasked on the plated side. On immersion in

600 mM sodium chloride solution, changes in the open circuit potential were monitored relative to a saturated calomel reference electrode placed 1cm from the surface of the test electrode. A data logger was used to record the variation in potential over a period of up to 1000 hours.

Galvanic corrosion studies

The compatibility of the electrodeposited zinc-nickel coatings with 2014-T6 aluminium alloy was assessed by monitoring the galvanic current developed when coated test panels were connected to a 2014-T6 aluminium alloy test panel and immersed in 600 mM sodium chloride solution 10cm apart and parallel to each other. The coated test panels were prepared in the same way as for the total immersion studies. The galvanic current was measured using a zero resistance ammeter and recorded with a data-logger. Measurements were continued for times up to 600 hours.

Results and Discussion

Exposure to neutral salt fog

Previously published work on the corrosion behaviour of electro-deposited zinc-nickel coatings has largely concentrated on steel substrates. The time to the appearance of red rust is normally used as a measure of the ability of the coating to protect the substrate and there is general agreement that under exposure to continuous neutral salt fog, coatings containing 12-15% nickel provide the greatest level of protection. In the present study the substrate was an aluminium alloy similar in composition to material widely used in the manufacture of electrical connector shells. An assessment of the performance of zinc-nickel coatings was made, by comparing the nature of the corrosion pitting which occurred on exposure to neutral salt fog.

From metallo-graphic sections, the pit density, the mean pit depth and the mean size of the largest pits found were determined. The data for single and dual layered coatings are reproduced in Table 4, including the numbers of pits greater than 8 microns. These have penetrated the coating and resulted in localised attack of the substrate.

Table 4   Analysis of pit depth data for single and dual-layer coatings

	Single layer coatings			Dual-layer coatings		
	4%Ni	10%Ni	17%Ni	5/10	10/14	5/14
Total no. of pits / mm	12.65	16.85	19.70	5.63	4.11	5.89
Number of pits >8μm / mm	5.12	8.33	12.85	2.52	1.01	1.71
Mean pit depth, μm	12.8	23.2	16.5	18.8	8.7	15.3
Mean of deepest pits, μm	38.6	136.8	62.8	51.2	8.9	51.5

The total number of pits recorded on the single layer coatings was considerably higher than for the dual-layer coatings and the number of pits penetrating through the coating into the substrate was also much greater. Table 4 further shows that the 10/14 dual layer coating was particularly effective in protecting the substrate. It was further observed that less corrosion products were formed on the high nickel coatings. This is important for electrical connector applications.

Corrosion behaviour under total immersion conditions

The results of experiments conducted to measure the variation in potential with time for selected single layer coatings, are reproduced in Figure 2. The initial potential is dependent on the nickel content of the coating, with increased nickel levels resulting in more noble coatings. This is shown by the plots in Figure 3, where the potentials after 10 hours immersion are plotted as a function of the nickel content. For each of the coatings in Figure 2, there is an increase in potential with time that is due to the loss of zinc from the coating. This continues until a potential between -0.70 and -0.74 volts (wrt SCE) is reached. The plots show many negative surges in potential indicating localised corrosion activity.
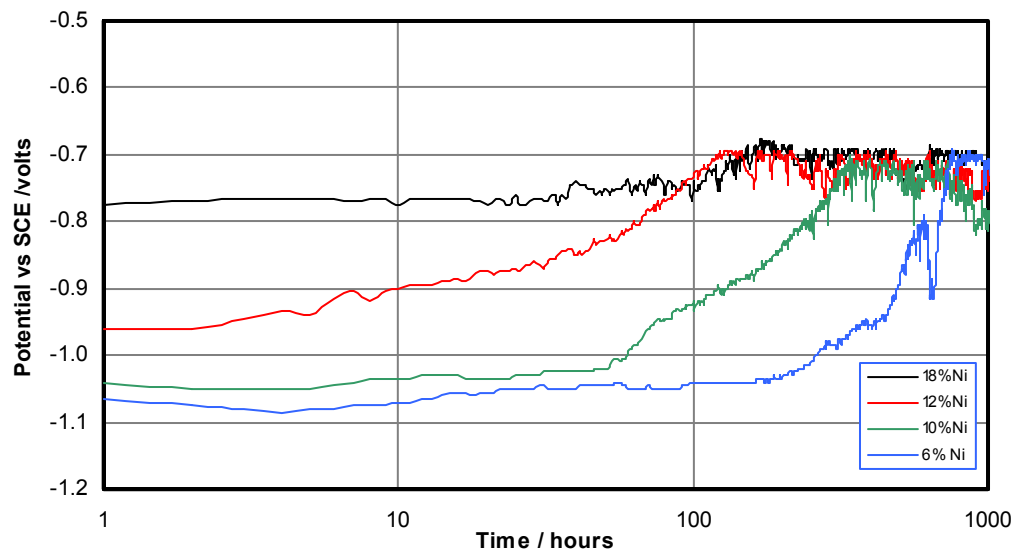
Figure 2   Variation on corrosion potential with time for single layer zinc-nickel coatings electrodeposited onto 2014-T6 aluminium alloy and immersed in 600mM sodium chloride solution.
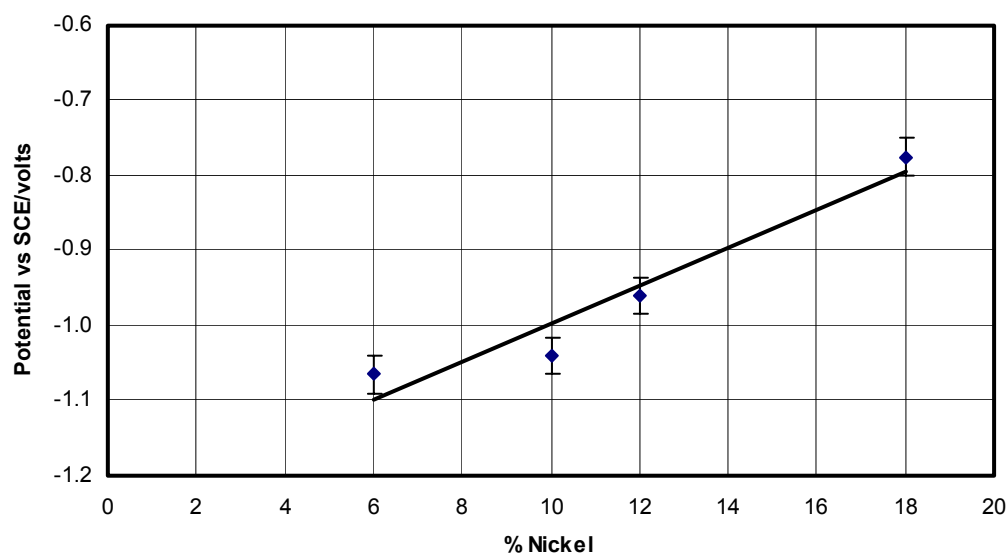

Figure 3   Effect of nickel content on the corrosion potential of zinc-nickel coatings electrodeposited onto 2014-T6 aluminium alloy and immersed in 600mM sodium chloride solution. Measurements made after 10 hours immersion.

Measurements were made on an unprotected 2014-T6 aluminium alloy panel immersed in 600 mM sodium chloride solution. The alloy adopted a potential of -0.73 volts (wrt SCE) but with increasing immersion times many negative surges in potential were recorded.

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This is consistent with the formation of corrosion pits on the exposed surfaces.

The potential, determined for the 2014-T6 aluminium alloy, is similar to the potential reached by the single layer coatings after long immersion times. This suggests that at this point the coatings are no longer giving protection.

The potential-time curves for the dual-layered coatings are reproduced in Figure 4. Overall the behaviour of the three dual-layered coatings appear similar to those for the single layer coatings. However the times at which the potential starts to stabilise are significantly longer. Thus comparing the single layer zinc-10%nickel coating with the dual layer coating Zn-5%Ni/Zn-10%Ni, estimates made from the potential – time data indicate that the time is increased from 330 hours to 700 hours. A similar effect is observed with the Zn-5%Ni/Zn-14%Ni coating compared with a single layer, zinc-high nickel coating.
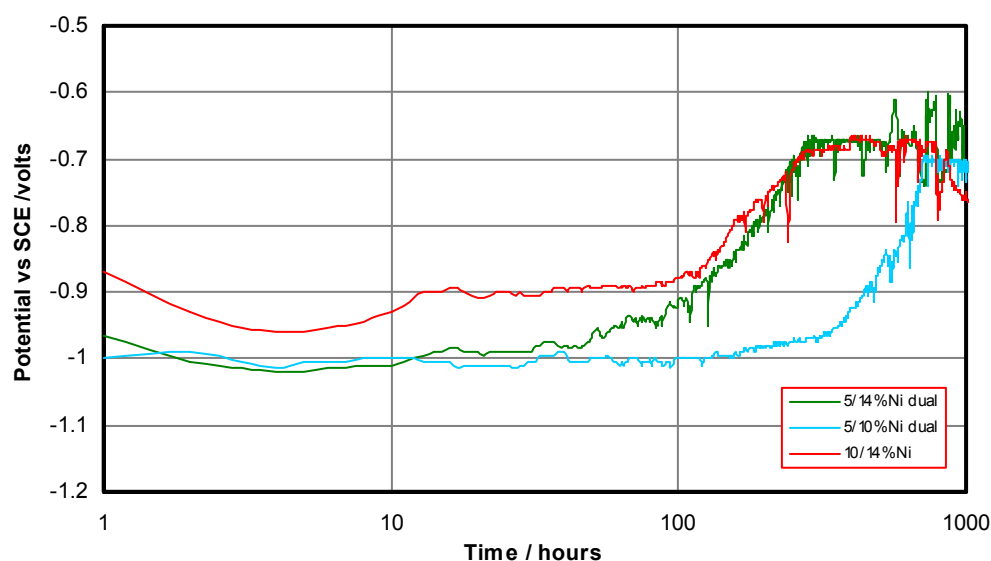
Figure 4   Variation in corrosion potential with time for dual–layered zinc–nickel coatings electroplated onto 2014–T6 aluminium alloy and immersed in 600mM sodium chloride solution

Galvanic corrosion

Galvanic corrosion current measurements were made to compare the sacrificial behaviour of the different coatings deposited and to determine their compatibility with structural aluminium alloys.

Figure 5 shows the variation in galvanic current with time for two single layer coated panels coupled to 2014–T6 aluminium alloy coupons. The zinc–14% nickel coating exhibited a reversal in current flow after 556 hours immersion. This is associated with the loss of zinc from the coating, eventually making the coating more noble than the aluminium alloy. At this point the coating ceases to protect the alloy and instead the alloy gives sacrificial protection to the coating. In contrast the low nickel coating continues to give protection throughout the duration of the test.
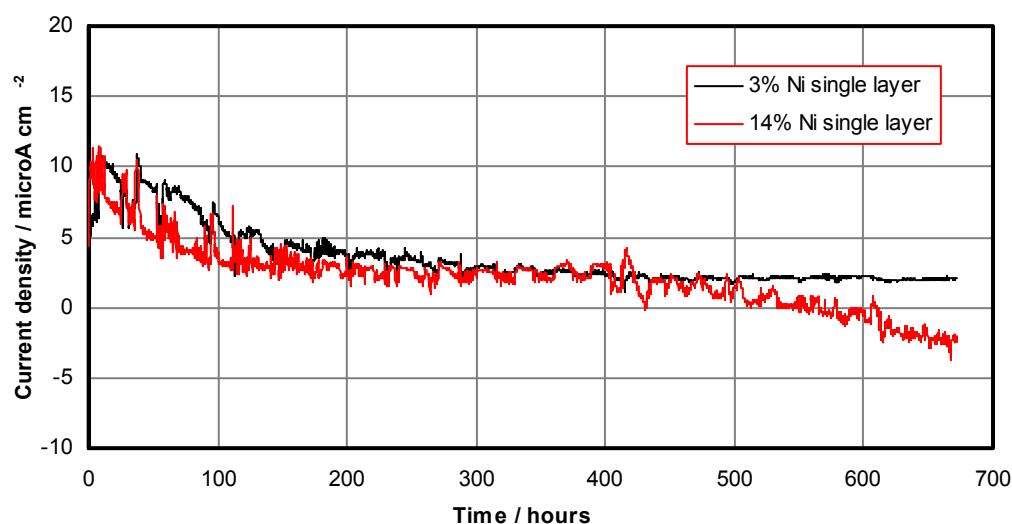

Figure 5   Variation in galvanic current with time for single zinc–nickel coatings electroplated onto 2014–T6 aluminium alloy coupled to 2014–T6 aluminium alloy and immersed in 600mM sodium chloride solution

The three dual–layered coatings examined also showed current reversal. This may be seen from Figure 6. The degree to which the

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coating is corroded is directly related to the electrical charge that has passed. This may be calculated from the plots in Figures 5 and 6 for each of the coatings investigated. Table 5 compares the total charge after 100 hours, 200 hours and at the point of current reversal (CR), for each of the coatings.
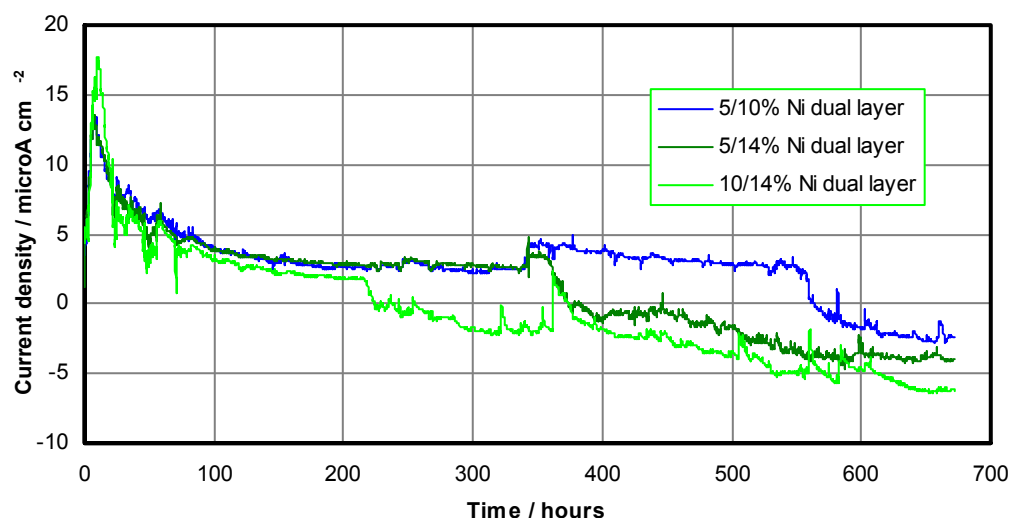

Figure 6   Variation in galvanic current with time for dual–layered zinc–nickel coatings electroplated onto 2014–T6 aluminium alloy coupled to 2014–T6 aluminium alloy and immersed in 600mM sodium chloride solution

Table 5   Galvanic corrosion

Coating	Total charge after 100 h (C cm^{-2})	Total charge after 200 h (C cm^{-2})	Time to CR (hours)	Total charge at CR (C cm^{-2})
Zinc – 3% Ni	2.86	4.46	670*	8.5*
Zinc – 14% Ni	2.20	3.30	556	5.7
Dual Layer 5 /10	2.45	3.58	553	7.5
Dual Layer 5/14	2.31	3.48	374	5.2
Dual Layer 10/14	2.22	3.07	256	3.3

The electrochemical behaviour of the dual-layer coatings appears to be related to the total nickel content of the coating. As the nickel content is increased, the time to current reversal is decreased. The results in Table 5 show that the coatings become increasingly more sacrificial as the nickel content is reduced. Hence to achieve a high level of protection if the coating is damaged a coating with a low nickel content should be selected. In contrast for galvanic compatibility with structural components made from aluminium – copper alloys, coatings which generate small but positive galvanic currents are required. Table 5 indicates that the coatings with zinc-14% nickel layer give the best performance. This is in agreement with the results discussed by Alexis et al. [#ref04].

Dual-layer coatings for connector applications

The neutral salt spray tests have demonstrated that the dual-layer coatings, in particular zinc – 10% nickel / zinc – 14% nickel, provide a higher level of protection against localised corrosion than single layer coatings of equivalent thickness. The potential – time data and the galvanic corrosion studies have further shown that the dual layered coatings are sacrificial in nature and will hence protect the substrate if the coating becomes damaged. The electrochemical measurements made on dual-layer coatings indicate that the selection of a coating with a zinc-14% nickel outer layer will give galvanic compatibility with aluminium alloys. Further studies are required to determine the galvanic compatibility with cadmium plating and the electrical properties of the coatings.

Conclusions

Under neutral salt fog conditions, dual-layered zinc nickel coatings have been shown to be more effective in protecting 2014-T6 aluminium alloy than single layer coatings

In 600mM sodium chloride solution, both single and dual-layer zinc-nickel coatings undergo de-zincification, leading to an increase in the

open circuit potential on continued immersion. For single layer coatings, the initial potential is dependent on the nickel content of the coating.

Galvanic corrosion measurements indicate that all the coatings examined will provide sacrificial protection to the 2014-T6 aluminium alloy substrate. To ensure good compatibility with structural aluminium alloys, coatings with a higher nickel content should be selected to reduce the level of galvanic corrosion occurring and to minimise the level of corrosion products

The dual-layer coatings provide an improved resistance to localised corrosion, act as sacrificial coatings and are compatible with structural aluminium alloys.

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