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PII: S0257-8972(08)01040-2
DOI: doi: 10.1016/j.surfcoat.2008.11.003
Reference: SCT 14717

To appear in: *Surface & Coatings Technology*

Received date: 25 August 2008
Accepted date: 4 November 2008

Please cite this article as: U. Bardi, S. Caporali, M. Craig, A. Giorgetti, I. Perissi, J.R. Nicholls, Electrodeposition of aluminium film on P90 Li-Al alloy as protective coating against corrosion, *Surface & Coatings Technology* (2008), doi: 10.1016/j.surfcoat.2008.11.003

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# ELECTRODEPOSITION OF ALUMINIUM FILM ON P90 Li-Al ALLOY AS PROTECTIVE COATING AGAINST CORROSION

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**Abstract**

In this paper we report on the electrodeposition of thin aluminium layers on P90 lithium-aluminium alloy at room temperature from a chloroaluminate ionic liquid (1-butyl-3-methyl imidazolium heptachloroaluminate $[BMIm]Al_2Cl_7$). We found that the treatment of the P90 sample's surface is a key point to obtain good quality coatings. On freshly mechanically polished surfaces, thin (about 24μm), homogeneous and dense aluminium layers were obtained at $10\mu m.h^{-1}$ deposition rate. Finally, the corrosion resistance of the uncoated and Al-coated samples was investigated by means of electrochemical techniques such as electrochemical open-circuit potential, impedance spectroscopy and potentiodynamic polarization in 3.5 wt% NaCl aqueous solution.

We found that the protective aluminium layer significantly reduces the corrosion rates of the P90 Li-Al alloy.

***Keywords:*** Ionic Liquids; electrodeposition; lithium-aluminium alloy; Corrosion; XPS.

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## 1. Introduction

The research of increased stiffness, but low-density material is a key point for several industries especially for aerospace, since structural weight reduction is a very efficient means of improving aircraft performance. The research of more advanced materials with high specific properties is therefore mandatory for such industry. Li-Al alloys are among the candidate materials because the addition of lithium to aluminium reduce the overall alloy's weight (1 wt% Li added to Al reduces the density by 3%) and increases the elastic modulus. Furthermore, fatigue crack resistance in Al-Li alloys is high; allowing the use of such alloy as important structural material. In contrast to new materials systems such as fibre-reinforced composites, Li-Al alloys do not require large capital investments in new fabricating facilities, resulting in being more cost effective than composites in some applications. However, these materials exhibit poor corrosion resistance, suffering several types of degradation (exfoliation, pitting, intergranular and intersubgranular corrosion, etc..) that strongly limits their usage in hostile environments [1]. The reason for such corrosion weakness is mainly due to the presence of precipitate phases such as $Al_3Li$ that are characterised by a different potential with respect to the surrounding matrix, driving localized corrosion phenomena. The corrosion resistance of Li-Al alloys can be improved using chromate conversion layers or corrosion inhibitors such as rare earth salts [2]. However, these treatments are toxic or expensive, especially taking into account the recycling cost of the materials so treated at the end of their service life. In order to find a non toxic and cost effective way to improve their corrosion properties, this study considers covering the surface with a pure aluminium layer capable of shielding the precipitate phases from aggressive environment and therefore avoiding the onset of corrosion. The advantage of using an aluminium coating is principally due to 3 main factors: (1) It is a lightweight metal, therefore it does not increase the overall density significantly, (2) its crystalline structure is very similar to the substrate avoiding lattice's

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mismatch that in some cases could drive the detachment of the coatings, (3) aluminium is a primary alloy element, therefore the material can be easily recycled without any purification process. Lab-scale electrodeposition of aluminium from ionic liquids has been known for a few years [3-6] and recently commercial metals and alloys such as mild steel, brass and magnesium have been successfully Al-plated [7-9]. It has been also demonstrated that the coatings obtained from ionic liquid electroplating bath can effectively enhance the corrosion resistance of the substrate materials [9,10] owing to the ability of aluminium to form a stable oxide film on its surface. To the best of our knowledge electroplating of Li-Al has never been attempted, principally for the difficulties to remove the oxides layer that spontaneously form on the surface. In this work we present the results of our attempt to obtain homogeneous aluminium layer on P90 Li-Al alloy. Finally, we obtained good quality coatings and, for the first time, we investigated the corrosion properties of such composite materials via electrochemical techniques. The results were compared with bare P90 alloy and pure aluminium.

## 2. Experimental

The material studied is a commercial Al-Li alloy (namely P90) whose composition is 2.96% Li, 0.04% Fe, 0.089% Zr and Al balance. From a bar (16 mm diameter) thin disks were cut (4 mm thick) and polished with SiC paper down to 1200 grit in order to achieve a smooth and reproducible surface. The plating process was carried out inside a nitrogen filled glove box (Iteco mod 10A), where the water and oxygen content was kept below 5 ppm. The electroplating bath was constituted by 1-butyl-3-methyl-imidazolium heptachloroaluminate [BMIm]$Al_2Cl_7$ (BMImCl÷$AlCl_3$ molar ratio 1÷2), supplied by Merck and used as received without further purification. The deposits were produced in current controlled (galvanostatic)

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conditions at room temperature, using an anode of pure aluminium foil (Goodfellow 99.9%). Once the electroplating process was terminated the samples were cleaned, inside the glove box, with acetone (Normapur, VWR Prolabo) in order to remove the main part of the ILs, and then cleaned in open air with several rinses of deionised water. The morphology of the coatings was investigated by optical (Nikon Eclipse LV150) and Scanning Elecron microscopy (ISI 100B), while the chemical composition was determined by Energy Dispersive X-Ray Microanalysis (EDX) and X-ray photoelectron Spectroscopy (XPS). The EDX measurements were obtained using a NORAN NSS 300 detector fitting the peaks with Gaussian type curves, applying the Proza (Phi-Rho-Z) correction method. XPS experiments were performed in an ultra-high vacuum ($10^{-9}$ mbar) system equipped with a VSW HAC 5000 hemispherical electron energy analyser at 90° respect to the sample, and a non-monochromatized Al-Kα X-ray source (1486.6 eV). The source power was 300 W (15 kV×20 mA) and the spectra were acquired in the constant-pass-energy mode at Epas = 44 eV. The overall energy resolution was 1.2 eV as a full-width at half maximum (FWHM) for the Ag $3d_{5/2}$ line of a pure silver reference. No neutralizer was utilized and the spectra energy scale was corrected using the adventious C 1s peak (284.8 eV). The recorded spectra were fitted using XPSPeak 4.1 software. Gauss-Lorentz curves were used to fit the data after subtraction of a Shirley-type background.

The electrochemical characterization was performed using a potentiostat PAR model 2273 controlled by PowerSuite 2.58 software. The cell used was a EG&G PARC Flat Cell using the three electrode set-up with the working electrode surface of 1.0 $cm^2$, a Pt grid and a standard calomel electrode (SCE) were used as counter (CE) and reference (RE) electrodes respectively. The RE was separated from the solution with an ion conducting glass frit. The corrosion experiments were carried out at room temperature (20±2ºC) in aerated 3.5 wt% NaCl solution. All the samples were kept in the saline solution for at least 20 h before carrying

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out the impedance (EIS) and potentiodynamic polarization (PD) experiments in order to allow the stabilization of the system. During this time the open circuit voltage (OCV) was recorded. The EIS spectra were measured in the frequency range between 1 MHz and 10 mHz, sampling twenty frequencies per decade, at the OCV, applying a sinusoidal perturbation of ±10mV. The PD curves were recorded starting from -0.250 V respect to the OCV at the scan rate of 0.3 $mVs^{-1}$.

## 3. Results and discussion

### *3.1. Sample surface's treatment.*

Due to the high reactivity of the metals constituting the alloy in the atmospheric conditions, the sample's surface is characterised by the unavoidable presence of an oxidation layer. In figure 1 is shown the wide scan XPS spectra, obtained on a 1200 grit polished P90 samples. Apart from the adventious carbon, always presents in samples exposed to atmosphere, the sample's surface is constituted by aluminium, lithium, carbon and oxygen. (see also the insets of figure 1). The binding energy values of these peaks, summarised in table 1, are consistent with the presence at the surface of aluminium oxides/hydroxides and lithium carbonate. The thickness of such layer is quite high, at least higher than the probe depth of the technique (about 6 nm at 1450 eV [13]), as argued by the absence of the signal attributable to metallic Al. Attempts to deposit aluminium onto these samples always resulted in inhomogeneous coatings. Aluminium grew only as islands scattered on the surface, leaving the main part of the sample unplated (figure 2). Surface treatments, performed outside the glove box, aimed to remove this layer were attempted but proved useless. If exposed to air, in few seconds, the alloy is capable of forming an alteration layer thick enough to prevent the homogeneous electrodeposition. Electrochemical etching, carried on directly in the ionic liquid inside the

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glove box, were attempted by applying a positive potential (up to 1V vs pure Al wire as reference) for times varying from 20 second up to 2 minutes, but the results were also not satisfactory. Instead, polishing the samples by 1200 SiC paper inside the glove box, leaves the surface clean enough to allow the electrodeposition of a dense, homogeneous and well adhering aluminium layer (figure 3a and 3b).

***3.2 Characterization of the Al coatings***.

In order to avoid possible corrosion of the alloy by the Al(III) the electrodeposition process was carried out immediately after the immersion of the sample in the electroplating bath and continued for two hours at constant current density (10 $mA.cm^{-2}$). These conditions proved to represent a good compromise between the electroplating time and the coating's quality. Infact, shorter time lead to the formation of too thin a coating while, due to the preferential growth of some crystallographic faces, the roughness of the deposits strongly increases with the amount of aluminium electrodeposited [10]. The coating is shown to be quite adhering to the substrate as determined by passing the sellotape strip test, and their thickness was evaluated by cross sections examination (see the figure 3a) as 24±4 μm. Edge effects were observed but these relative effects were negligible, never exceeded 20%. EDX analyses of the coatings, (figure 3c), are characterised by the presence of only two peaks; the main one attributable to the aluminium and a second one, barely detectable, to the oxygen. Peaks due to the contribution of others elements, such as chlorides, that were expected to be present as contaminations deriving from the electroplating bath, are not detectable, therefore their content is under the detection limit for this technique, in accordance with the previously obtained results on

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similar ionic liquids [7-10] permitting us to infer the coating constituted almost pure aluminium.

### *3.3 Electrochemical corrosion tests*

The effectiveness of the coatings as corrosion protection against wet corrosion was then extensively examined by OCV, EIS and potentiodynamic polarization measurements in aerated 3.5 wt% NaCl aqueous solution.

#### *3.3.1 Open circuit voltage curves*

The open circuit voltage curves (OCVs) were recorded as a function of time for up to 20 hours of immersion time in order to achieve a stable value. Figure 4 shows examples of the curves obtained for the pure aluminium (a), the Al-plated (b) and the bare P90 alloy (c) respectively. The curves obtained on pure Al and Al-plated P90 samples are characterised by an initial period of time where the potential shifts towards a more negative value. This behaviour, typical for aluminium in contact with chloride containing solution [14] has been attributed to the degradation of the alumina layer via the formation of nanopores and the adsorption of $Cl^-$ ions [15,16]. The induction time varies between 2 and 8 hours, probably due to the slightly different thicknesses and degrees of hydration of the alumina layer spontaneously formed as soon as the Al is exposed to air. After this time the potential reached almost a constant value of -1.0V for the pure Al and -1.15V for the Al-plated P90. Vice versa, the shape of the curves recorded on the bare P90 sample is much less defined (fig 4c). After an initial shift towards more negative value analogous to the previously depicted, the potential remains randomly oscillating, even after several hours of exposition (Figure 4c) indicating a more active

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behaviour. However, also for the P90 sample is possible to identify a plateau close to the value of -1.25V vs. SCE. This value is more negative than the pure aluminium, and the Al-plated, confirming the thermodynamic tendencies of the P90 alloy to be corroded and, at the same time demonstrate that the thin pure aluminium coating significantly contributes to mitigate this effect.

*3.3.2 Impedance spectra*

The EIS data for these samples were recorded to further evaluate their corrosion resistance. In figure 5a is shown the Bode plots for the Al-plated P90, compared to the bare alloy and pure aluminium. The coated samples display behaviour very close to the pure aluminium while the uncoated sample shows a much lower resistance. A better insight into the corrosion properties of the coating can be achieved by plotting this data in the form of Nyquist diagrams (figure 5b). The experimental data show an arc-like behaviour over the frequency range examined and the diameter of the semicircles increase from the bare P90 (detectable only in the inset of figure 5b) to the Al-plated and pure aluminium samples. These measures unequivocally show the polarization resistance (Rp) increases for the Al-coated samples, which in turn, is associated with a decrease in corrosion rate [17].

*3.3.3 Potentiodynamic polarization curves*

Some other important information, such as the ability of the material to spontaneously passivate, the potential region over which the specimen remain passive and the corrosion current density ($i_{corr}$) can be obtained from the recording of the potentiodynamic polarization (PD) curves. Examples of these curves of both the plated and unplated P90 samples are shown in figure 6 compared with pure aluminium. As previously pointed out for the OCVs, it can be seen that the curves obtained on pure aluminium and the Al-plated P90 samples, even thought

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slightly variable in the absolute value, are characterised by a similar shape, indicating, on the whole, close analogies in the corrosion behaviour for these samples. These curves present a wide passive region extending from the corrosion potential ($E_{corr}$) to nearly -0.7V, characterised by a relative small anodic dissolution current, followed by a sudden rising of the current, due to the breaking down of the alumina protective layer and the start of pitting corrosion. This behaviour has been already reported in literature for aluminium alloys and can be considered typical for aluminium in chlorides solution [10, 18, 19].

Accordingly to the OCV curves the corrosion potential shifts towards more negative value starting from the pure Al samples to the Al-plated and the bare P90 sample that presents the most negative corrosion potential value (-1.2V vs. SCE). The corrosion current density ($i_{corr}$), was qualitatively extrapolated superimposing a straight line along the most linear portion of the PD curve. The interception of this line at the corrosion potential gives the $i_{corr}$ value (see the example displayed in the inset of figure 6). For these measures we chose to consider only the cathodic branch because in the anodic one the surface is changing due to the corrosion process. Bare P90 samples always shown the highest corrosion current density (about 17 $\mu A.cm^{-2}$) while the pure aluminium and the Al-plated P90 were characterised by values of about one order of magnitude lower (table 2). The reason of the variability between pure Al and Al-plated P90 samples is related to the sample's surface roughness variability. As previously reported [10] the surface of the deposits, electrochemically grown from this type of ILs, are quite rough and the roughness quickly increase with the amount of deposed metal. For coatings of about 24 μm this phenomenon is still moderate, however, the increase in the exposed surface due to the enhanced roughness is not neglectable. Unfortunately, it is not possible to accurately control this characteristic; therefore the evaluation of the corrosion current can be deduced only qualitatively. In the light of these considerations, the little differences between the Al and Al-plated P90 samples that have been presented are not be

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considered to be significant. In contrast, the current for the bare P90 samples always results to be about one order of magnitude higher. Therefore, even if the $i_{corr}$ are not directly comparable because the exposed surface for the plated samples can not be measured and therefore is unknown, this data demonstrates that the P90 sample in contact with NaCl solution undergoes more rapid anodic dissolution while in the Al-plated case this process is strongly reduced, behaving almost like pure aluminium.

## 4. Conclusions

The present work shows that the corrosion resistance of P90 aluminium–lithium alloy can be greatly improved by coating the material with a thin layer of pure aluminium electroplated from ionic liquid. From the 1-butyl-3methyl imidazolium heptachloroaluminate electroplating bath it is possible to obtain, at room temperature, a homogeneous deposits of pure aluminium. If the sample's surface is prepared in an atmosphere where the water and oxygen content are kept below 5 ppm, the coating adheres well to the substrate, without the use of additives. The deposition rate achievable is about 10μm $hour^{-1}$. The results presented in this paper show, for the first time, the possibility of utilizing ionic liquids as electrochemical media to successfully obtain an effective corrosion resistant coating on lithium aluminium alloys, an extremely interesting material that is now scarcely employed in industry due to its poor corrosion resistance.

**Acknowledgements**

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Financial support from the European Community (Project FP6-(STREP) Contract Number: 517002, IOLISURF) is gratefully acknowledged.

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**References.**

[1] S. A. Nugent, Conference - Australasian Corrosion Association (1991), 31st (Corrosion 91), Paper F07, 14 pp

[2] B. Davò, J.J. De Damborenea, Electrochimica Acta, 49 (2004) 4957

[3] S. Takahashi, N. Koura, S. Khoara, M. L. Saboungi, L. A. Curtiss, Plasma & Ions 2, (1999) 91

[4] L. Simanavicius, A. Stakenas, A. Sarkis, Elect. Acta 46 (2000) 499

[5] C. L. Aravinda, I. Mukhopadhyay, W. Freyland, Phys. Chem. Chem. Phys. (2004), 6, 5225

[6] C.L. Aravinda, B. Burger and W. Freyland, Chem. Phys. Lett. 434, 4-6 (2007), 271

[7] T. Jiang, M.J. Chollier Brym, G. Dubé, A. Lasia, G.M. Brisard, Surf. Coat. Techn., 201 (2006), 1

[8] Q. X. Liu, S. Zein El Abedin, F. Endres, Surf. Coat. Tech., 201 (2006) 1352

[9] J.-K. Chang, S.-Y. Chen, W.-T. Tsai, M.-J. Deng, I.-W. Sun, Electrochem. Comm. 9 (2007) 1602

[10] S. Caporali; A. Fossati, A. Lavacchi, I. Perissi, A. Tolstogouzov, U. Bardi, Corr. Science, 50 (2008) 534.

[11] Contour, J. P., Salesse A., Froment M. Garreau M. Thevenin J., Wari D. J. Microsc. Spectrosc. Electron. 4, (1979) 483

[12] J. F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Physical Electronics Division, 1992.

[13] J. F. Watts and J. Wolstenholme, *An Introduction to Surface Analysis by XPS and AES*, Wiley, Chichester, 2003

[14] E. M. Sheriff, Su-Moon Park, Electrochim.Acta 51 (2006) 1313

[15] F.J.Martin, G.T.Cheek, W.E. O'Grady, P.M. Natishan, Corr Science 47 (2005) 3187

ACCEPTED MANUSCRIPT



[16] B. Zhang, Y. Li, F. Wang, Corr Science 49 (2007) 2071

[17] N. Perez , *Electrochemistry and Corrosion Science*, Kluwer Ed. , Norwell USA, (2004)

[18] W.A. Badawy, F.M. Al-Kharafi, A.A. El-Azab, Corros. Sci. 41 (1999) 709

[19] N. Sato, Corros. Sci. 37 (1995) 1947

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**Figure captions.**

**Fig. 1.** XPS survey spectra of a polished sample. Only peaks attributable to carbon, oxygen, aluminium and lithium are detectable. The insets shows the detailed regions of C, Al and Li.

**Fig. 2.** SEM micrograph of an aluminium deposit obtained in current constant condition (10 $mA.cm^{-2}$) onto a P90 sample chemically etched.

**Fig. 3.** Cross sectional optical microgaphs (a) and SEM image of the surface (b) and EDX analysis (c) of the Al layer electrodeposed on P90 alloy.

**Fig. 4.** Open circuit potential curves (OCVs) as a function of time of pure Al (a), Al-plated P90 (b) and bare P90 (c) samples. The curves are recorded in aerated 3.5 wt% NaCl solutions at room temperature.

**Fig. 5.** EIS spectra (Bode plots (a), Nyquist plots (b)) of the Al-plated P90 sample compared with the pure aluminium and the bare P90 alloy in 3.5 wt% NaCl solution. In the inset of figure 6b shows the detail of the curves at very high frequencies.

**Fig. 6.** Potentiodynamic anodic polarization curves (scan rate $0.3mVs^{-1}$) of pure Al (a), Al-plated P90 (b) and bare P90 (c) samples. The curves are recorded in aerated 3.5 wt% NaCl solutions at room temperature. The inset shows the evaluation of $i_{corr}$ for the bare P90 sample.

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Fig 1

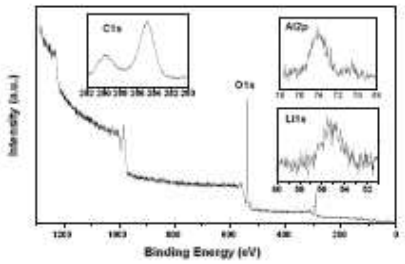


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Fig 2

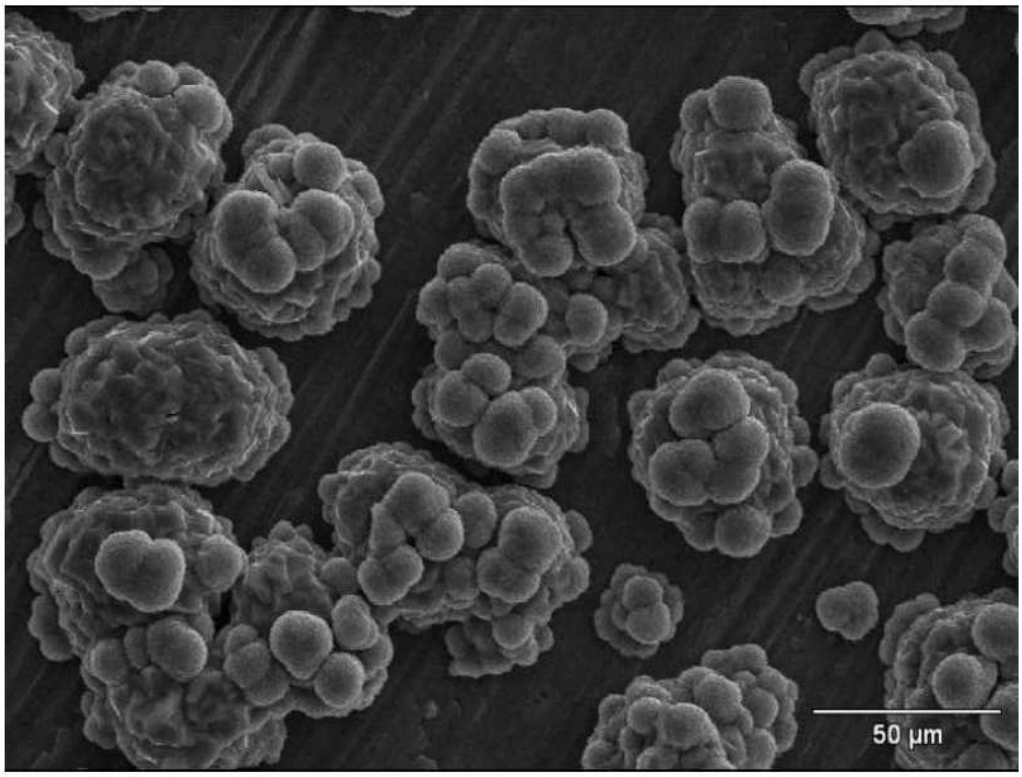


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Fig 3

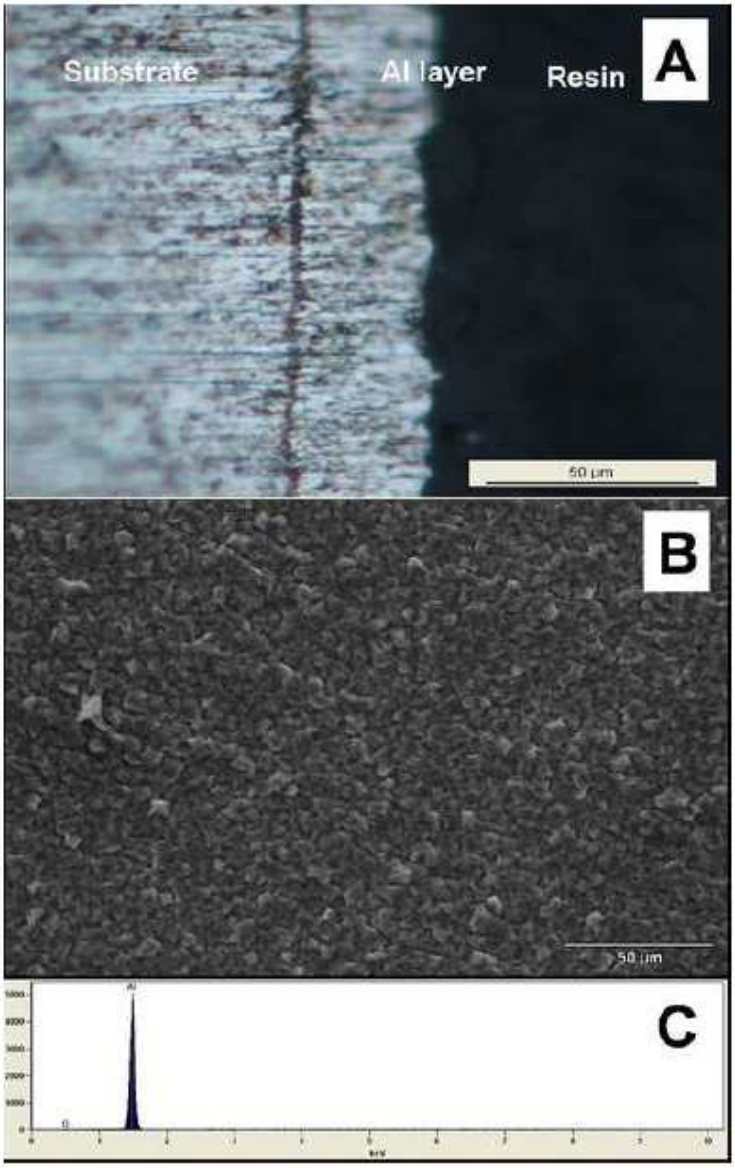

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Fig 4

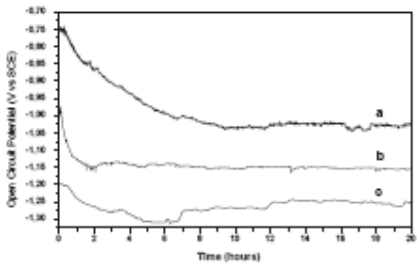


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Fig 5a

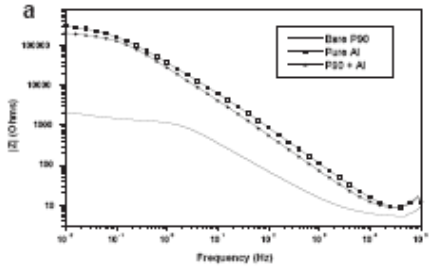


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Fig 5b

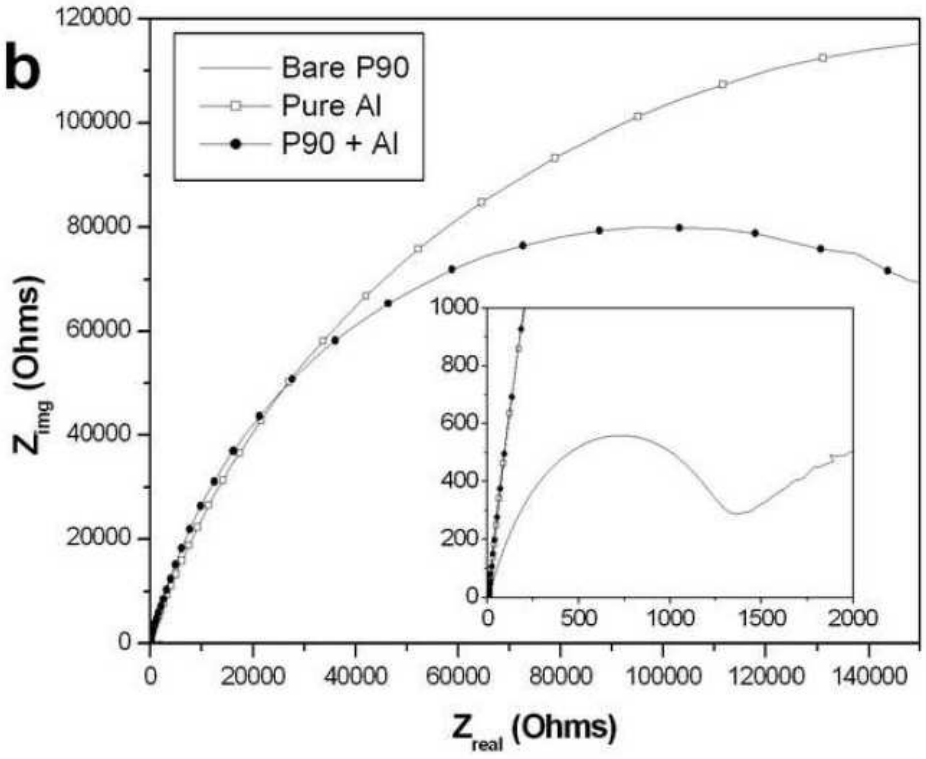


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Fig 6

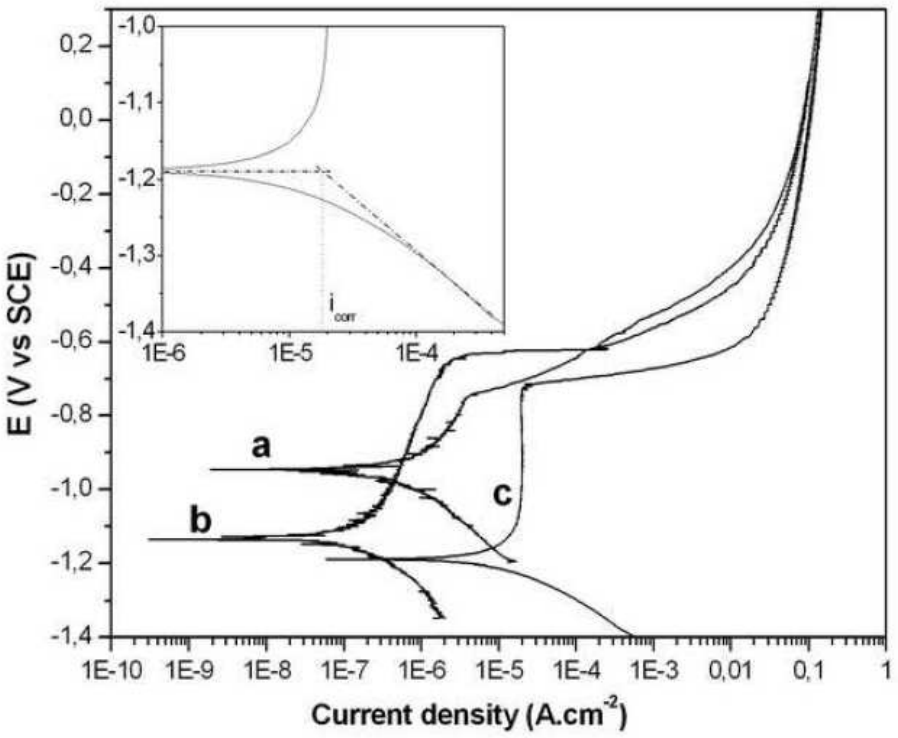


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**Table 1**. XPS data of the P90 Li-Al alloy surface.

| Elements | Binding Energy (eV) | Attribution | Reference |
|---|---|---|---|
| **O** | 531.3±0.1 | 1s O oxides/carbonate | [11] |
| **C** | 284.8±0.1 | Atmospheric contamination | [11] |
| | 289.7±0.1 | 1s C in $Li_2CO_3$ | [12] |
| **Li** | 55.2±0.1 | 1s Li in $Li_2CO_3$ | [12] |
| **Al** | 74.2±0.1 | 2pAl oxides/hydroxydes | [11] |

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**Table 2**. Electrochemical corrosion data of the bare P90 Li-Al alloy and the Al plated compared with the pure aluminium.

| Material | Corrosion current density ($\mu A.cm^{-2}$) | Corrosion Potential ($E_{corr}$) (V vs.SCE) |
|---|---|---|
| **P90** | 17 ± 3 | -1.20±0.01 |
| **P90 20µm Al plated** | 0.5±0.5 | -1.13±0.02 |
| **Pure Al** | 1.0±0.5 | -0.95±0.02 |

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**2009-02-28T00:00:00Z**
Elsevier Science B.V., Amsterdam.
http://dx.doi.org/10.1016/j.surfcoat.2008.11.003
U. Bardi, S. Caporali, M. Craig, A. Giorgetti, I. Perissi, J.R. Nicholls, Electrodeposition of aluminium film on P90 Li-Al alloy as protective coating against corrosion, Surface and Coatings Technology, Volume 203, Issues 10-11, 25 February 2009, Pages 1373-1378,

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