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Aluminium electroplated from ionic liquids as protective coating against steel corrosion

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Abstract

The protective action of thin layers of aluminium electroplated on a carbon steel (UNI Fe360B) has been studied. The coatings were obtained via electroreduction, at room temperature, from an ionic liquid constituted by 1-butyl-3-methyl-imidazolium heptachloroaluminate. Coatings of different thickness, ranging from 10 to 40 μm, were obtained. Their morphology and chemical composition were investigated using SEM microscopy coupled with EDX microanalysis and X-ray diffraction. Electrochemical tests (potentiodynamic polarization curves, open-circuit potential and electrochemical impedance spectroscopy) were performed in order to characterise the corrosion resistance of the coating in 3.5% NaCl aqueous solution. Visual investigation of the samples during long term of exposition to neutral salt spray gave an evaluation of their free corrosion properties. It was found that the aluminium layers deposited from ionic liquids significantly protect the substrate from the general corrosion and this action increases with the coating thickness.

Keywords: A. Ionic liquids; A. Aluminium; C. Corrosion; B. Polarization curves; B. Electrochemical impedance spectroscopy

1. Introduction

Aluminium is an important material with a strategic role in several industrial applications owing to its excellent physical and mechanical properties as well as the outstanding corrosion resistance. Therefore, this metal is becoming a key material in many applications such as for the automotive industry, aviation, household appliances heat exchangers and ship building [1,2]. The corrosion resistance of aluminium arises from its ability to form a natural oxide film on its surface that greatly reduces the corrosion rate [3]. Unfortunately, aluminium plating is a very challenging task. The electrodeposition of this metal from aqueous solution is impossible due to the hydrogen discharge and high vacuum techniques such as chemical vapour deposition (CVD) and physical vapour deposition (PVD) are slow and very expensive. Electrodeposition from molten salts is widely used for aluminium production (process Heroult–Hall) but the high temperature required, higher than the aluminium melting point, makes this process useless for plating. At the same time hot dipping does not permit a good control of the coating thickness.

Ionic liquids (ILs) are a relatively new class of compounds characterised by high conductivity, extremely low vapour pressures, low viscosity, low toxicity, non flammability, high thermal stability, wide electrochemical window and being liquid in a wide range of temperatures [4,5]. These properties make such compounds ideal media for the electroreduction, at room or close to room temperature, of highly electropositive metals which cannot be electrodeposited from aqueous media [6]. In ILs, the electroreduction of pure aluminium and aluminium alloys has been recently obtained by several groups [7–10]. In this

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paper we report the results of an investigation of the protection against corrosion played by aluminium layers applied on a commonly used carbon steel (UNI Fe360B). The aluminium coatings were obtained at room temperature from 1-butyl-3-methyl-imidazolium heptachloroaluminate ([BMIM]Al_2Cl_7). The corrosion properties of such composite materials were evaluated both via electrochemical techniques and cabinet salt spray tests and the results were compared with the bare carbon steel and the pure aluminium.

2. Experimental

From a commercial grade bar (15 mm diameter) of UNI Fe360B carbon steel (nominal composition: $C\% < 0.17$, $Mn\% < 1.40$, $P\% < 0.045$, $S\% < 0.045$ and Fe balance), two different series of samples were prepared. For the electrochemical tests thin coupons were cut (4 mm thickness) and polished with SiC paper down to 1200 grit in order to achieve a smooth and reproducible surface. Just before the aluminium electroplating, the coupons were chemically polished as described by Liu and co-workers [10] in order to remove the oxides and the organic impurities eventually present on the surface. The second series of samples was made in the form of cylinders (about 80 mm length and 15 mm diameter) and used for the salt spray test. After machining and cleaning, these samples were aluminium plated for about 3/4 of their length. The parts left unplated were covered with epoxy resin (see Fig. 7). The average roughness of the surfaces was measured using a Hommel Tester W55. The measurements were obtained performing five different and independent tests in randomly chosen areas of the sample. The measures were performed scanning 4.8 mm of surface at 0.2 mm s^{-1} of scan rate. The parameters employed were $\lambda c = 0.8$ mm and $\lambda c/\lambda s = 300$ using a filter ISO 11562(MI), for every type of sample the R_a, R_z and R_t values were calculated. 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 galvanic bath was constituted by 1-butyl-3methyl-imidazolium heptachloroaluminate ([BMIm]Al_2Cl_7), supplied by Merck and used as received without further purification. The deposits were obtained in current controlled (galvanostatic) conditions at room temperature using as anode a pure aluminium foil (Goodfellow 99.9%). More details about the aluminium electrodeposition and the electrodes preparation can be found in the literature [10]. The morphology of the coatings was investigated by optical (Nikon Eclipse LV150) and scanning elecron microscopy (ISI 100B), while the chemical composition and the surface phases were obtained, respectively, by energy dispersive X-ray microanalysis (EDX) (NORAN NSS 300) and X-ray diffraction analysis (Bragg–Brentano configuration, Cu K_α radiation). The EDX peaks were fitted by Gaussian type curves applying the Proza (Phi-Rho-Z) correction method. The diffraction spectra were analysed by means of a fitting program based on the Rietveld method (Rietquan 2.3).

The electrochemical characterisation was performed using a Model K47 corrosion cell from Princeton Applied Research. The potentiostat was a PAR model 2273 controlled by PowerSuite 2.58 software. The classical three electrode set-up was employed using two high-density graphite counter electrodes and a SCE reference electrode separated from the solution with an ion conducting glass frit, the working electrode surface was 1.0 cm^2. The experiments were carried out at room temperature (19–23 °C) in a saline solution obtained dissolving NaCl (>99.5% from Merck) in deionised water. Every sample was kept in the saline solution for at least 14 h in order to allow the stabilization of the system. During this time the open-circuit potential (OCV) was recorded. After this time, electrochemical impedance spectroscopy (EIS), and potentiodynamic (PD) experiment were performed. The EIS spectra were measured in the frequency range between 100 kHz and 5 mHz, sampling 20 frequencies per decade, at the free corrosion potential, applying a sinusoidal perturbation of ±10 mV. The PD curves were recorded starting from −0.250 V respect to the free corrosion potential at the scan rate of 0.3 mV s^{-1}. Free corrosion tests were conducted in a salt spray cabinet (Angelantoni model DCTC600 P) spraying NaCl solution (50 ± 5 gr dm^{-3}) at 35 ± 2 °C (NSS test). The evolution of the corrosion phenomena was monitored by visual investigation up to 75 days.

3. Results and discussion

3.1. Chemical and physical characterisation of Al coatings

After accurate surface cleaning as described in Ref. [10], the carbon steel samples were electroplated with aluminium layers of three different thicknesses. The electroreduction process was carried out at constant current density (10 mA cm^{-2}) and controlling the time of deposition. In this way, we obtained three series of samples for 1, 2 and 4 h of deposition, respectively. In these conditions the yield for the electrochemical reduction of aluminium was nearly 100% as demonstrated by the coating thickness resulted. The thickness was evaluated by cross-sections examination (see Fig. 1a–c) and resulted 12 ± 1, 24 ± 2 and 40 ± 5 μm for the samples obtained after 1, 2 and 4 h of deposition, respectively. Edge effects were observed but their relative effect was negligible (especially for the lower thickness samples) and it never exceeded the 15%. From the sequence of SEM images shown in Fig. 1 is also evident that roughness increases with thickness. An accurate quantification of this phenomenon was obtained by means of profilometric measurements, performed as described in experimental part. The results are summarised in Table 1. All the roughness parameters dramatically increase with the time of deposition, however the largest effect was observed for Ra. The reasons of this behaviour are connected with the increase

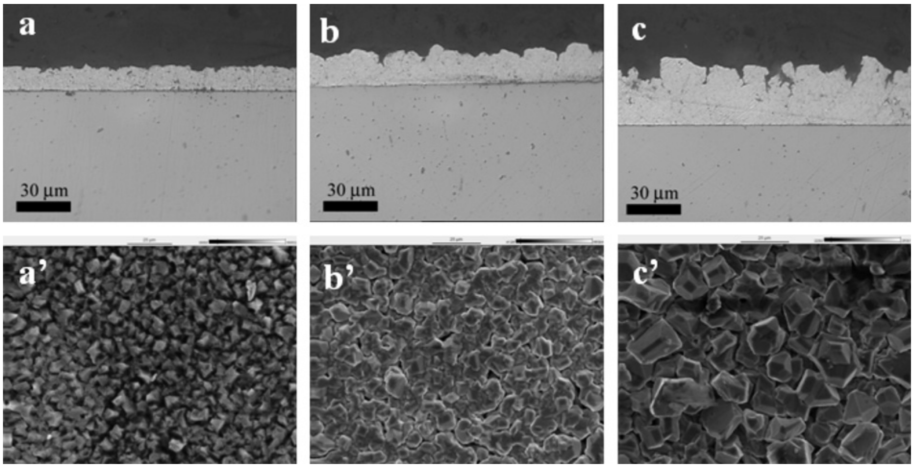

Fig. 1. Optical micrographs of the cross-sections obtained from the carbon steel samples coated with aluminium layers. The samples named "a" are obtained after 1 h deposition, "b" after 2 h and "c" after 4 h. The pictures named a', b' and c' are the SEM micrographs of the respective coating surfaces.

Table 1
Roughness parameters measured on the aluminium coated sample surfaces compared with the polished Fe360 substrate

Sample	Parameters		
	Ra (μm)	RzISO (μm)	Rt (μm)
Fe360 substrate	∼0.1	0.7 ± 0.1	1.2 ± 0.6
Fe360 + ∼10 μm Al coating	0.6 ± 0.1	5.4 ± 0.7	8.7 ± 1.5
Fe360 + ∼20 μm Al coating	1.0 ± 0.1	8.0 ± 1.1	10.6 ± 2.1
Fe360 + ∼40 μm Al coating	2.5 ± 0.1	18.3 ± 1.4	24.3 ± 0.7

of the average crystal size and the preferential orientation of the grains constituting the deposits.

The second series of photos displayed in Fig. 1a'–c' show the morphologies of the three types of deposits. The coatings obtained after 1 h deposition are characterised by small size grains (<5 μm), while in the coatings obtained in longer deposition time, the average size tend to increase. Comparisons between the XRD spectra obtained for all the three type of samples show that the coatings are constituted by pure Al fcc phase but, while initially the grains are almost randomly oriented on the surface (Fig. 2a), as the time of deposition increases, we observe a preferential growth of the crystalline grains. In particular, in the spectrum in Fig. 2a the intensity of the {2 0 0} family of planes is comparable with that one of the {1 1 1} family. In the other cases, the signal due to the {2 0 0} becomes dominant (Fig. 2b and c). This observation is consistent with a preferential growth of the {2 0 0} oriented faces in comparison to the other crystallographic orientations.

3.2. Electrochemical corrosion tests

3.2.1. Open-circuit voltage curves

Open-circuit potential curves (OCVs) were recorded in aerated 3.5 wt% NaCl aqueous solution as a function of time. In Fig. 3 we show the OCV curves obtained for the three different aluminated samples compared with the bare carbon steel and the pure aluminium (this sample was obtained from the same type of aluminium foil used as anode in the plating process and described in the experimental part). The bare carbon steel samples show a shift of the potential towards more negative values reaching the almost constant value of about −0.70 V/SCE after

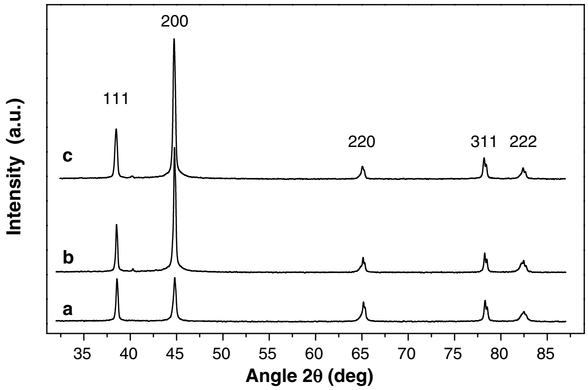

Fig. 2. XRD spectra of the aluminium deposits obtained after 1 h (a), 2 h (b) and 4 h (c) deposition, respectively.

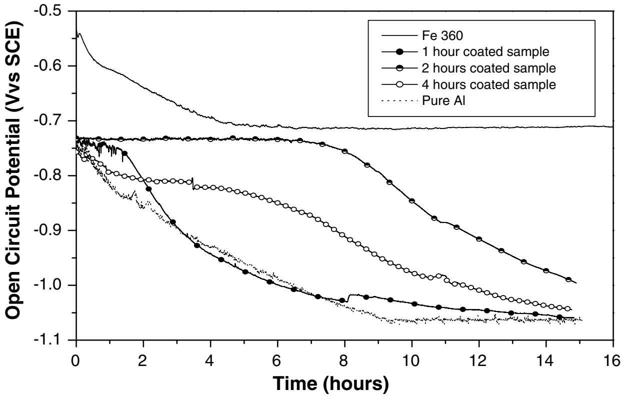

Fig. 3. Open-circuit potential curves (OCVs) of different thickness aluminium coated samples compared with the bare carbon steel and the pure aluminium in 3.5 wt% NaCl aqueous solution as a function of time.

5 h. The aluminated samples are characterised by an initial period where the potential remains almost unchanged, followed by a shift towards more negative potentials. This behaviour, very close to that of pure aluminium, can be related to the change of the surface due to the degradation of the thin aluminium oxide layer present on the sample and removed in the chloride containing solutions in agreement with the following reaction [11]:

$$\mathrm{Al}^{3+}_{\text{(in crystal lattice of the oxide)}} + 2\mathrm{Cl}^- + 2\mathrm{OH}^- = \mathrm{Al(OH)_2Cl_2^-} \tag{1}$$

However, the potentials of the aluminated samples are always more negative than the bare carbon steel, indicating the protective action of the coatings respect to the substrate.

3.2.2. Impedance spectra

The EIS experiments were performed just after the OCV recording, in order to further evaluate the sample's corrosion resistance. In Fig. 4a we show the Bode plots relative to the different coated samples compared to the bare carbon steel and the pure aluminium. The coated samples display an intermediate behaviour between the carbon steel and the aluminium. A better insight in the corrosion properties of the coating can be achieved plotting these data in the form of Nyquist diagrams (Fig. 4b). The experimental data show an arc-like behaviour over the frequency range examined which suggest that in these condition corrosion of the samples occurred. Notice from Fig. 4b that the diameter of the semicircle increases from the bare carbon steel to the aluminated and pure aluminium samples. This implies that the polarization resistance (R_p) also increase with the amount of aluminium deposed onto the carbon steel, which in turn, decreases the corrosion rate of the sample [12]. This observation indicates that the aluminium coating led to an effective improvement in corrosion resistance and this effect is directly related with the thickness of the coating.

3.2.3. Potentiodynamic polarization curves

Further insight into the corrosion properties was obtained via potentiodynamic measurements (PD). Fig. 5 shows a series of curves in aerated 3.5% NaCl solution, of the three different coatings compared with bare carbon steel and pure aluminium.

As observed before, the unplated carbon steel samples show the highest free corrosion potential (nearly −0.70 V), while all the aluminium bearing samples are characterised by rather lower value (between −0.90 and −1.05 V). Furthermore, these samples are characterised by a very slow increase of the cathodic current up to about −0.75 V where a sudden rising up of the anodic current is observed. This increase is correlated to the break down of the aluminium coating and the start of pitting corrosion [13–15]. Cyclic polarization experiments (Fig. 6) were carried on to evaluate the passive region for such system in chloride solution. In such experiments the scan direction is reversed at a predetermined potential leading a cathodic polarization until the reverse curve intersects the forward scan. The intersection is located at about −0.80 V; a value that can be considered the limits for the resistance of the system to the pitting corrosion.

Once the pitting corrosion is started, the anodic current value is higher in the Al coated samples than in the bare carbon steel (Fig. 5). In these conditions the protective action of the aluminium coating is lost and both the

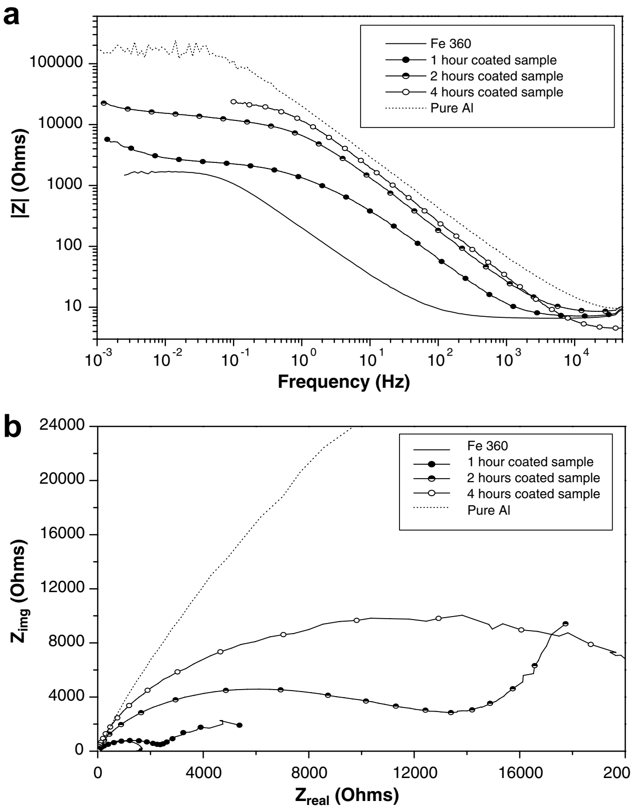

Fig. 4. EIS spectra (Bode plots (a), Nyquist plot (b)) of different thickness aluminium coated samples compared with the pure aluminium and the bare carbon steel in 3.5 wt% NaCl solution.

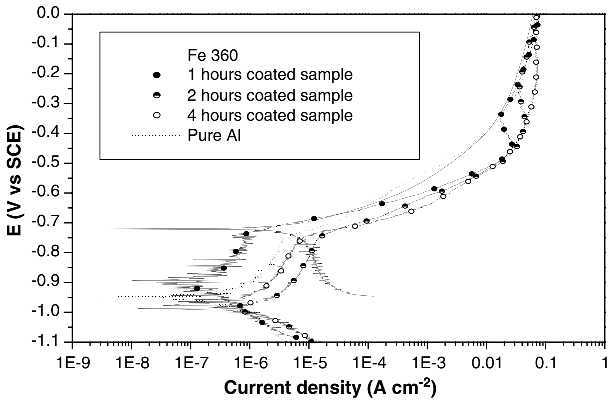

Fig. 5. Potentiodynamic curves (scan rate 0.3 mV s^{-1}) of different thickness aluminium coated samples compared with the pure aluminium and the bare carbon steel in 3.5 wt% NaCl aqueous solution.

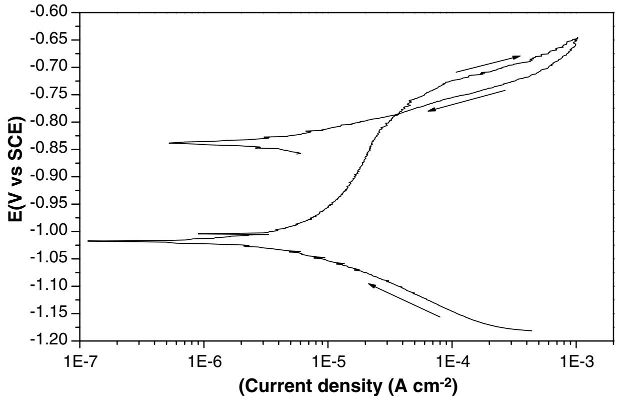

Fig. 6. Cyclic polarization curve (scan rate 0.3 mV s^{-1}) of an aluminium plated sample of carbon steel (UNI Fe360B) in 3.5 wt% NaCl aqueous solution.

remaining aluminium coating and the exposed substrate surfaces actively contribute to the anodic current values. This condition remains up to the complete removal of the coating where a decrease of the corrosion current is detectable and there are no more differences between the curves obtained between plated and unplated samples.

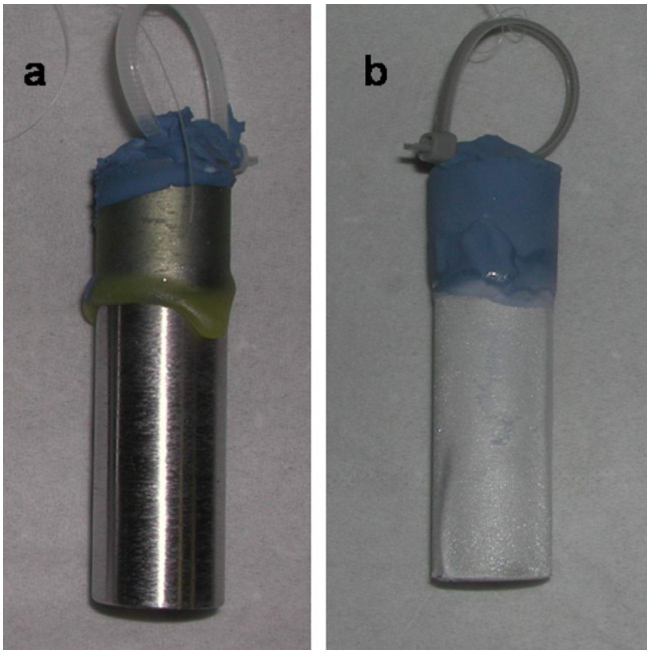

Fig. 7. Sample prepared and ready to be placed in the spray chamber. The picture "a" is relative to the bare carbon steel used as benchmark, "b" illustrates an aluminium coated sample. The uncoated part is protected from the saline solution by epoxy resin.

3.3. Neutral salt spray (NSS) test

A series of bare carbon steel (Fig. 7a) and the three series of coated samples (Fig. 7b) were prepared as described in the experimental part and placed in the salt spray chamber up to 75 days. During this time the evaluation of the different corrosion degree was obtained by visual investigation. After just 1 day the carbon steel samples were completely covered by corrosion products (Fig. 8d). On the contrary, the coated samples did not show any corrosion feature up to several days of exposure. The first spots of corrosion were detected after 5 days on the 10 μm-coated samples (Fig. 8a) as few small rusty-red points. These spots tend to increase in number and dimensions with the time of exposure (Fig. 8b). These samples after two weeks shown corrosion features in about one half of the total exposed surface, (Fig. 8c), while after 30 days the coating results completely removed. The samples characterised by thicker aluminium layers demonstrate a better corrosion resistance; the first corrosion features for the samples 20 μm aluminium coated were observed after 8 days, while the

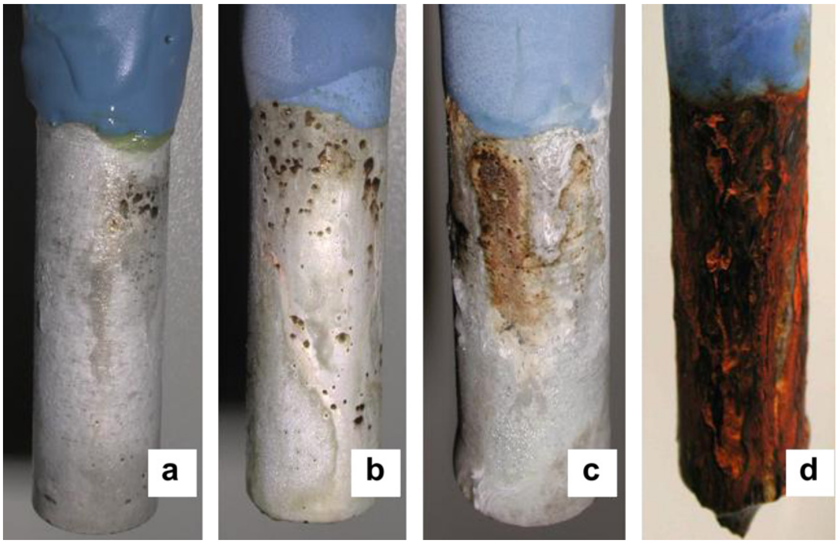

Fig. 8. Sequence of images showing the process of degradation for a carbon steel sample coated with 10 μm of aluminium during the NSS test. The pictures are taken, respectively, after 5 (a), 8 (b), 14 (c), 30 (d) days of exposure.

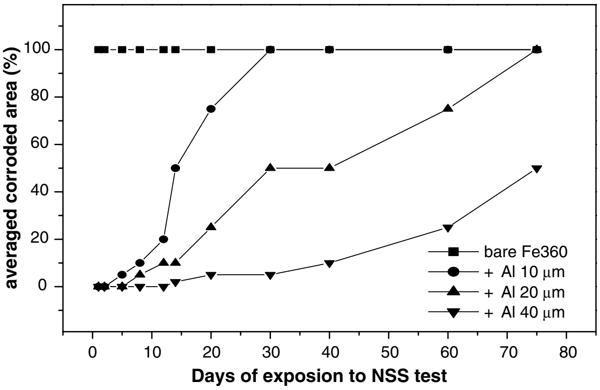

Fig. 9. Salt spray test corrosion kinetics for the aluminium coated carbon steel. The different coating thicknesses were compared with the bare carbon steel (UNI Fe360B).

40 μm coated remain unaffected up to 14 days of exposure. The evolution of the corrosion spots was the same for all the samples, but the presence of thicker aluminium layer contribute to the slowing down of the corrosion process. As a result, the complete removal of the 20 μm coating take about 70 days of exposition, while at the end of the experiment (75 days) the samples coated with 40 μm of aluminium shown only about the 25% of the coating removed. In Fig. 9 are graphically summarised these results.

4. Conclusions

The present work shows that aluminium coatings electrochemically deposited from ionic liquids at room temperature are an effective protection of carbon steel against wet corrosion. Thicker coatings turned out to be more effective than thin ones. In all cases, the protection failed thorough a pitting mechanism. Future studies will be focused on the use of additives or the samples post treatment in order to obtain more homogeneous and effective aluminium coatings. However, already the present results show the possibility of utilizing ionic liquids as electrochemical media for coating processes of industrial relevance.

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