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Absorption of water and corrosion performance of a clear and pigmented epoxy coating on Al-2024 alloy

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Abstract

The corrosion performance of Al-2024 substrates coated with an epoxy clear coating and a pigmented epoxy coating was investigated. The absorption of water in the pigmented coating was high compared to the clear coating. The clear coating provided a good barrier which is stable beyond 120 days of immersion in a 0.5 M NaCl solution. The shape of the Nyquist plot of the pigmented coating changed with immersion time and reveals the existence of physico-chemical processes in the coating and/or at the interface. Its impedance magnitude at low frequencies remained very high ($\sim 10^9$ $\Omega.cm^2$) after 72 days of immersion in sodium chloride solution. Both coatings exhibited good dry adhesion on Al-2024. The wet adhesion of the clear coating was poor while the stress (~ 9 MPa) required in a pull off adhesion test of the wet pigmented coating remained high.

1. Introduction

Aluminum alloy 2024 is a complex material containing numerous intermetallic compounds (IC). These compounds improve the strength and degrade the corrosion resistance of the material at the same time. The corrosion resistance decreases because of the formation of some complex galvanic couples between the IC and the surrounding Al-Cu solid solution or matrix (1, 2). Some of the compounds such as Al_2Cu and $Al_{20}Cu_2(FeMn)_3$ are cathodic, whereas others (Al_2CuMg) are anodic compared to the matrix (3). The corrosion inhibition of the aluminum alloy 2024 has been widely studied since this material is commonly used in aerospace applications. Presently, chromate-based systems provide the most efficient corrosion protection for this alloy (4, 5). However, chromate primers are toxic, carcinogenic, hence environmental unfriendly and their use as paints will progressively be abandoned.

Several investigations have been carried out towards the development of chromate free corrosion inhibitors for Al-2024. An alternative may come from the use of pigment and filler particles. For example, a Mg-rich primer was shown to provide equivalent or better corrosion protection on Al-2024 compared to the currently used chromate pretreatment plus chromate pigmented primer technology (6). The use of rare earth compounds gave promising results via direct immersion in rare earth salt solutions (5, 7) and coatings with rare earth contents (8-10). In general rare earth cations, especially Ce, were found to be a cathodic inhibitor on Al-2024 (5).

In the present work, the water solubility of a chromate free pigmented epoxy coating is compared with a clear epoxy coating. The corrosion performance of both coatings on Al-

2024 is studied by using electrochemical impedance spectroscopy. The aim is to understand the role that pigments and filler play in the mobility of water and charge transport in the coating and at the coating / alloy interface. For this reason, the microstructure of the coating / alloy interface as well as the wet and the dry adhesion of the coatings to the Al-2024 substrate are examined.

2. Experimental

The clear coating used in this work is a two component solvent free system comprising Epikote 828 epoxy and Jeffamine D230 as curing agent. In all formulations, the epoxy-to-amine stoichiometric ratio was 1/1 according to the manufacturer's specifications. The pigmented coating is a two-component chromate free primer supplied by AkzoNobel. This primer is an ambient cured epoxy / amine coating with an excess of bisphenol-A based epoxy. It contains 30 vol% pigment, no inhibitor and 350 g/l maximum volatile organic compliant. Both coatings were applied on Al-2024 substrates and a platinum foil depending on its further analysis. The coating thickness was about 70 ± 5 μm, where ± indicates the sample standard deviation.

For the microstructure of the pigmented coating, two pieces of Al-2024 coated with the primer were cut and embedded in a mixture of Technovit powder and a cold-curing resin for metallography testing. The coated sides were placed face-to-face to reduce the contact between the resin and the coating. The sample was ground and polished using 1μm diamond abrasive slurry. A thin film of carbon was evaporated on the polished section for electrical conduction and the sample was analyzed by using a JEOL JSM 840A Scanning Electron Microscope (SEM).

The Brasher-Kingsbury equation (11,12) was used to deduce the water volume fraction (ϕ_t) in the coatings from the capacitance versus time curve recorded after immersion of the coating in a 0.5 M NaCl aqueous solution;

$$\phi_t = \frac{\log\left(\dfrac{C_t}{C_0}\right)}{\log 80} \qquad [1]$$

where C_t is the coating capacitance at time t, C_o the capacitance of the dry coating, usually obtained by extrapolation to the instance of immersion and *80* is the value corresponding to the dielectric constant of water. Only coatings applied on platinum were used in order to avoid any reaction that might occur at the interface if electroactive substrates (such as the aluminum alloy 2024) are used.

Electrochemical impedance spectroscopy (EIS) was employed to monitor the corrosion behavior of the coatings (on Al-2024) in a 0.5 M NaCl solution. All data were recorded at room temperature using the Potentiostat / Galvanostat (EG&G, Model 283) coupled with the frequency response detector (EG&G, Model 1025).

Adhesion tests (pull off test) were also performed by using the Easy TEST (EZ 20) conventional tensile equipment. A stud of 8 mm in diameter was glued on the coating and allowed to dry. The epoxy glue (3M scotch-weld DP460) was selected because of its high strength. An electrical drill was used to remove the coating around the stud and the sample was mounted on the tensile equipment. The force (stress) needed to detach the coating from the substrate was monitored as a function of the stud displacement.

3. Results and discussions

3.1. Microstructure of the pigmented coating

Figure 1 displays the cross-section of the aluminum alloy coated with the pigmented primer. A thin oxide layer exists between the coating and the aluminum substrate. Using high magnification, it becomes clear that this oxide has a columnar structure with a thickness close to 2.5 μm. The coating contains different type of particles as shown by the differences in contrast of the lower part of figure 1b. The small and bright spots correspond to the non-conductive resin charged by the electron beam.
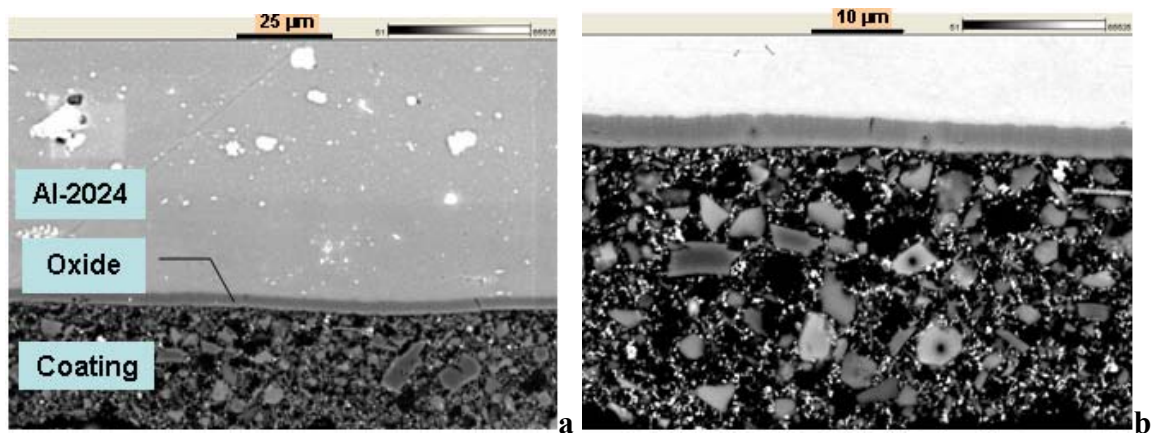

Fig. 1. Cross-section of the Al-2024 substrate coated with the pigmented primer. a) Overview of the sample showing the intermetallic inclusions in the alloy; b) magnification of the coating structure.

This small resin dust could have been introduced when the sample was imbedded and polished. Large filler particles with different contrast can be observed in figure 1b. The energy dispersive X-ray analysis of these particles reveals the presence of Si, Ti, and Al in the filler particles.

3.2. Water absorption in the clear coating versus pigmented coating

Water at the interface is often the main cause of corrosion, blistering and delamination of the organic coating from the substrate. For this reason, the transportation of water from the environment to the coating / substrate interface is of great interest to coating scientists. Measuring capacitance is one of the most suitable ways to monitor the water uptake of organic coatings with time. The principle is based on the difference in the dielectric constant between the organic coating ($1 \leq \varepsilon \leq 9$) and water ($\varepsilon = 80$). Any penetration of water in an organic coating will lead to an increase of its dielectric constant and hence its capacitance. The change of the coating capacitance with the immersion time allows the estimation of the water volume fraction (ϕ_t) by using equation 1.
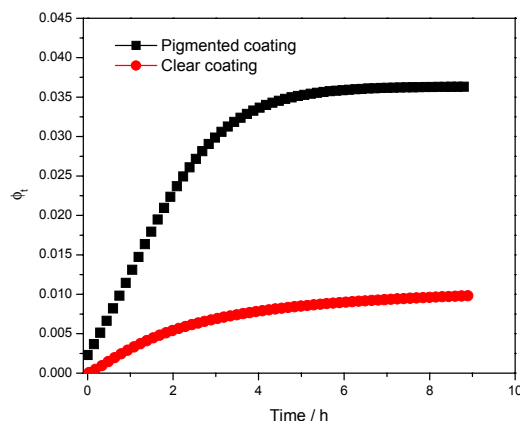
Fig. 2. Comparison of the water uptake for the clear and pigmented epoxy coatings.

Figure 2 shows the comparison between the water uptake of the clear coating and the pigmented coating. In both materials, the water volume fraction increases with the immersion time and reaches a steady value where no further water is absorbed. This level corresponds to saturation of the coating. Note that the water volume fraction at saturation (ϕ_s) is higher for the pigmented coating than for the clear coating. From this graph, the saturation level (often denoted as the solubility $S = \phi_s \, \rho_e$, where ρ_e is the density of water in Kg / m^3) of 35 kg / m^3 and 10 kg / m^3 can be derived for the pigmented and the clear coating, respectively. For an immersion time below 3 hours, the slope of the curve $\phi_t = f(t)$ is higher for the pigmented coating. This suggests that the diffusion coefficient of water in the coating containing filler and pigment is higher as compared to the clear coating. The higher diffusion coefficient and water solubility in the pigmented primer is attributed to the filler particles. A poor connection between the binder (epoxy matrix) and the filler in the network could lead to the formation of a small amount of free volume around the filler particles and could explain the high water solubility value observed in this case. Some of the filler particles might absorb water as well. On the other hand, the solubility values of both coatings are relatively low compared to some epoxy coatings where a water solubility value of about 40 kg / m^3 was found (13,14).

3.3. *Corrosion performance of the coatings evaluated by EIS*

The barrier property of the coatings was investigated by immersion in a 0.5 M NaCl solution. The impedance of the samples was recorded for various immersion times using a 10 mV amplitude of sinusoidal voltage. The Nyquist representation of the EIS data of the clear coating is displayed in figure 3.
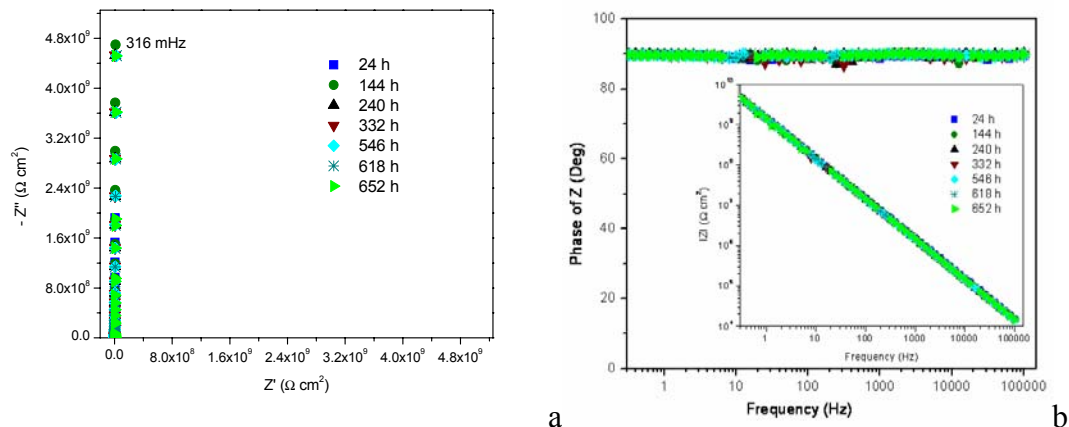
Fig. 3. Nyquist (a) and Bode plot (b) of the EIS data of the epoxy clear coating recorded in 0.5 M NaCl.

For the indicated period of immersion, the Nyquist plot of the impedance of the coating appears as a line perpendicular to the real axis and the coating impedance remains high at low frequencies. The phase angle is close to 90° in the whole frequency range and remains unchanged during the giving period of immersion. Such graph accounts for the capacitive behavior of the system and suggests that the clear coating exhibits a very good barrier property. Similar behavior was observed after 120 days of immersion.
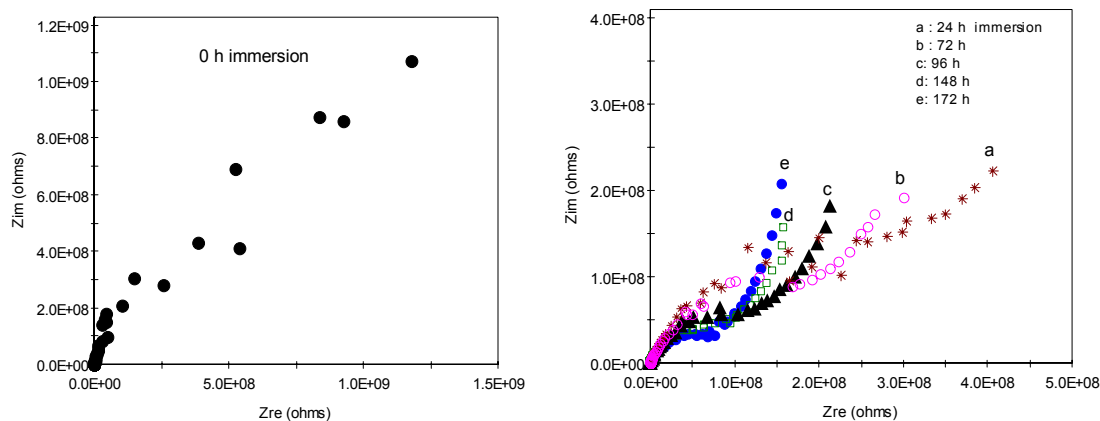

Fig. 4. Nyquist representation of the EIS data of the pigmented coating recorded in 0.5 M NaCl

The Nyquist plots of the impedance data of the pigmented coating are completely different from the clear coating where the capacitive behavior dominates the EIS spectrum. As depicted in Figure 4, a semi-circle can be observed on the spectrum of the pigmented coating at the initial stage (0 h) of immersion. Diffusion of water and oxygen seems to occur as shown by the line with a slope of approximately 45° with respect to the real axis at low frequencies. This suggests that a strict barrier type mechanism cannot account for the behavior of the pigmented coating.

From 24 to 72 h of immersion time, a semicircle appears at the high frequencies part and a line forming about 45° with the real axis dominates the low frequencies regime. This behavior is characteristic of an electrode process under diffusion and charge transfer control, suggesting that some reaction takes place in the coating and / or at the coating substrate interface. In the previous section, it was shown that the saturation of the coating with water occurs after 8 hours of immersion in a similar aqueous solution.

Between 96 and 172 h, a line nearly perpendicular to the real axis exists at very low frequencies while a line forming about 45° with the real axis appears at intermediate frequencies and a semi-circle at high frequencies. The kinetics change from charge transfer control to diffusion control at high and intermediate frequencies, respectively. At low frequencies, the effect of the finite diffusion layer becomes dominant and the Warburg impedance approaches the impedance of a capacitor as shown by the vertical line. This behavior could be due to the formation of a water and oxygen percolation path along the filler particles as the immersion time increases. Water and oxygen penetrate the coating and fill all free volume between the filler particles. The blocking of free volume and pores in the system could account for the capacitive tendency observed as the immersion time increases.

Despite the change of the shape of the Nyquist plot with time, the impedance magnitude remains very high at low frequencies, even after a very long period (72 days) of immersion. Furthermore, no visual degradation was observed in the pigmented coating after this period of immersion. This suggests that the presence of more water does not really alter the anticorrosive performance of the pigmented coating.

3.5. Wet and dry adhesion of the coatings on Al-2024.

The adhesion tests were performed by using the pull off test (detachment face of a stud glued on the coatings loaded perpendicular to the substrate). For the wet adhesion tests, the material was first immersed in distilled water for 24 h. From the water uptake versus time curves, it appears that this immersion time is sufficient to obtain saturation of the coating. In all cases, the tensile stress was measured as function of the stud displacement. The results are summarized in figure 5. Such experiments are useful to understand the extent to which coating disbonding will occur after water uptake.
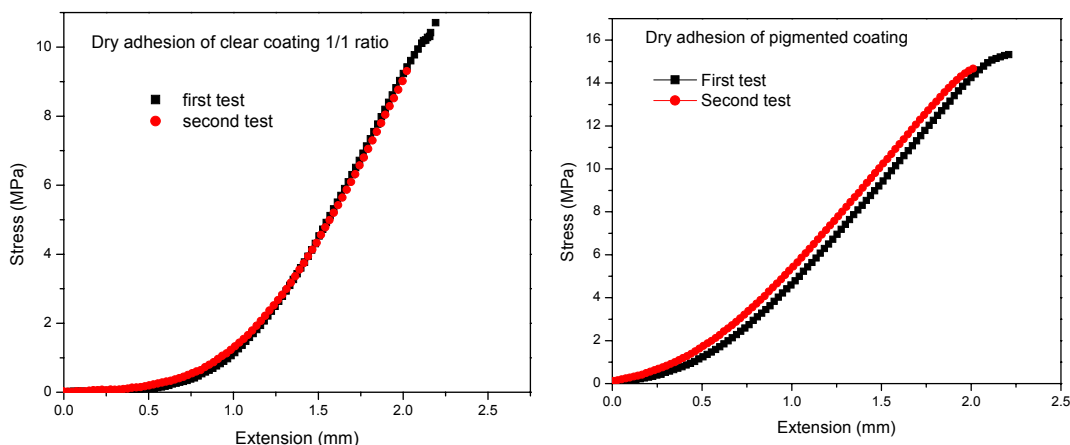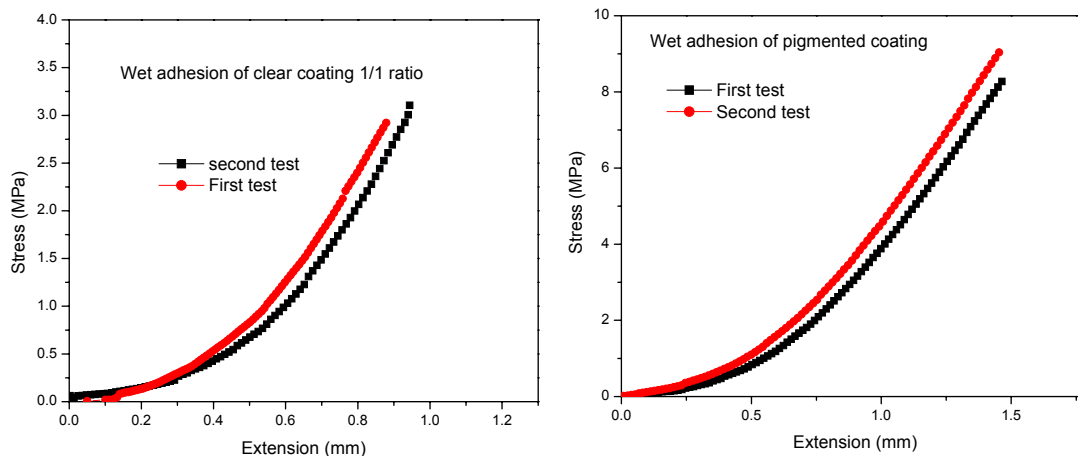
Fig. 5. Stress versus displacement obtained from pull off tests of the epoxy clear coating and a pigmented coating applied on the Al-2024 substrate. The diameter of the stud is ~8 mm.

Figure 5 shows that the stress required to pull off the dry coatings from the Al-2024 substrate is about 10 MPa and 15 MPa for the clear coating and the pigmented coating, respectively. Both values are relatively high, indicating that the adhesion of the coatings to the substrate is good. The higher stress (by a factor of 1.5 as compared to the clear coating) needed to remove the pigmented coating is probably due to the small excess of the epoxy component in its formulation.

After immersion of the coatings in distilled water for 24 hours, the stress required to pull off the clear coating from the substrate drops from 10 MPa to a value close to 3 MPa. As compared to the dry adhesion, the wet adhesion of the clear coating is poor. In contrast, the wet adhesion of the pigmented coating remains high as a stress of about 9 MPa is necessary to pull off these coatings.

For the pigmented coating, it is important to mention that the whole material below the stud did not delaminate from the substrate. This was also observed for both the wet and the dry adhesion tests. However, the clear coating was completely pulled off from the substrate. The force required to pull off completely the pigmented coating on an area close to the stud area (~50 mm^2) will be much higher. Micrographs of the stud and the coating after the adhesion test are displayed in figure 6.
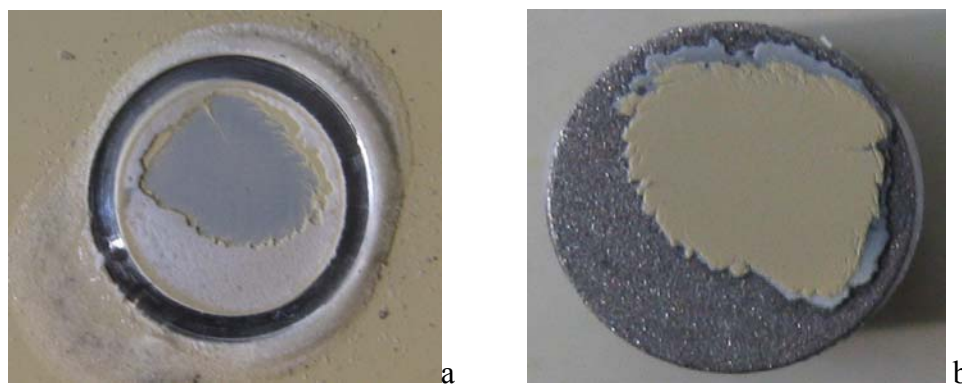

Fig. 6. Images of the Al-2024 substrate (a) and the stud (b) after the pull off test experi-

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ments. Both the dry and the wet adhesion tests on the pigmented coating exhibit similar crack behavior.

These images show clearly that only part of the coating under the stud is removed from the substrate. In most cases, the fraction of the coating that remains on the substrate constitutes about 45 % of the total stud area. The cracking morphology of the pigmented coating could be due to filler particles that make the coating stiffer.

4. Conclusions

An epoxy / amine clear coating and a pigmented epoxy coating were investigated. Scanning electron microscopy of the pigmented coating revealed the presence of different filler particles.
The diffusion coefficient and the absorption of water (solubility) in the pigmented coating were found to be quite high as compared to the clear coating. The behavior was assigned to the presence of small filler particles and to the existence of poor connection between the binder and the filler particles. This possibly leads to the formation of free volume around the filler particles and could also account for the higher water solubility and diffusion coefficient obtained for this type of samples.
Electrochemical impedance spectroscopy revealed good barrier property for the clear coating. The barrier property was stable above 120 days of immersion in a 0.5 M NaCl solution. The shape of the Nyquist plot of the pigmented coating changed with immersion time, showing that some physico-chemical process occurred in the coating and / or at the coating substrate interface. Nevertheless, the pigmented coating impedance magnitude remained high ($\sim 10^9$ Ωcm^2) at low frequencies even after 72 days of immersion in 0.5 M NaCl. The high water solubility did not affect significantly the anticorrosive performance of the pigmented coating.
 Both the pigmented and the clear coating exhibited good dry adhesion ($\sim$ 15 and 10 MPa, respectively) on the aluminum alloy 2024. However, the pigmented coating did not delaminate completely from the substrate. Cracking occurred in the coating and part of the material remained on the substrate. A wet adhesion stress of about 3 MPa obtained after 24 h immersion of the clear coating in distilled water was found to be relatively poor. The stress required to pull off the pigmented coating did not change significantly after immersion in distilled water.

Acknowledgements

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