The role of Mg²⁺ ions on the corrosion behavior of AA2024-T3 alloys immersed in chloride-containing environments

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Introduction

The replacement of chromate conversion coatings by hybrid sol-gel coatings doped with corrosion inhibitors has become a common practice in recent years. In the case of aluminum alloys, this practice is especially important due to their high susceptibility to pitting corrosion. Several studies have demonstrated the effectiveness of layered double hydroxides (LDHs), such as hydrotalcite compounds (HT). It is assumed that the way of action is based on their high anion-exchange capacity; therefore, these compounds could act as scavengers of aggressive chloride ions^{1,2}. That capability is strongly dependent on the nature of the compensating anion, being the lowest when it is carbonate. However, some studies³ have shown the improvement of the corrosion resistance of hybrid sol–gel coatings doped with hydrotalcite containing carbonate as the compensating anion (HT-CO₃), which means that an additional inhibition mechanism should exist. One aspect to consider is the chemical stability of HT with the (local) solution pH. In this sense, hydrotalcite dissolves in an acid pH, necessary to catalyze the sol-gel synthesis. Specifically brucite dissolves at pH around 5, incorporating the Mg²⁺ ions to the solution.

The present study deals with the effect of Mg^{2+} ions on the behavior of an AA2024-T3 alloy in the presence of chloride anions, especially dangerous for such alloys.

Experimental

The electrochemical measurements were carried out with an AUTOLAB® 30 Potentiostat (from EcoChemie). All the measurements were conducted with a threeelectrode arrangement at constant temperature (T=23 °C). The working electrode was the AA2024-T3 alloy with 0.3 cm² exposed area. The specimens were mechanically polished to 1 µm diamond paste. The reference electrode was an Ag/AgCl (3M KCl) with very low leakage $(10^{-9} \text{ L.h}^{-1})$, in order to avoid electrolyte contamination. The counter-electrode was a platinum mesh. Two different electrolytes were employed: 10mM NaCl solution or 5mM MgCl₂ solution, so that the chloride concentration remains constant. Polarization curves were performed from 150 mV below the E_{corr} up to reaching current density values in the order of mA.cm⁻², at 0.4 mV.s⁻¹ scan rate. The Electrochemical Impedance Spectroscopy (EIS) measurements were made using a sweeping frequency from 10^5 Hz down to 10 mHz with 10 points per decade and 3 mV rms signal amplitude. The measurements were made at the open circuit potential (OCP). In order to verify reproducibility, at least two samples were tested. The surfaces were examined using an Electroscan JSM-54 Scanning Electron Microscope (SEM) model JEOL 5410 equipped with an X-ray gun Link ISI 300 for chemical analysis by x-ray energy dispersion (EDX).

Results and Discussion

Figure 1 depicts the polarization curves for AA2024-T3 samples exposed to both types of solutions. The differences are evident: the presence of Mg^{2+} ions in the solution leads to a shift of corrosion potential towards more cathodic values, suggesting certain cathodic inhibition action. Besides, in the anodic domain a large plateau is observed between -0.74 $V_{Ag/AgCl}$ and -0.45 $V_{Ag/AgCl}$. That potential domain corresponds to low

current density, which indicates a passivation domain, not present in the solution without Mg^{2+} .



Figure 1. Polarization curves for 2024-T3 alloy in 10 mM NaCl (gray) and 5mM MgCl₂ (black) solutions.

Figure 2 shows the Nyquist plots of AA2024-T3 alloy after 19 hours of immersion in the studied solutions. The higher impedance values observed in presence of the Mg²⁺ corroborate their beneficial effect. At least two time constants can be observed in both diagrams. The high frequency time constant can be ascribed to the dielectric properties of the oxide/hydroxides generated on the metallic surface during the immersion period. The diameter of this semicircle is clearly higher in presence of Mg²⁺, indicating a higher compactness of this oxide film. The low frequency time constant can be related to the corrosion process. In the absence of Mg²⁺ it is possible to observe the low frequency limit at about 6 k Ω .cm². Nevertheless in the presence of Mg²⁺, no low frequency limit can be observed in the frequency window scanned. From the Nyquist diagram it follows also that the charge transfer resistance is clearly higher in the presence of Mg²⁺, that lead to slowdown of the corrosion process.



Both potentiodynamic experiments and impedance measurements have shown the effectiveness of Mg^{2+} as corrosion inhibitor for the AA2024-T3 alloys immersed in aggressive electrolytes. In order to clarify the possible mechanism of action, a morphological study by SEM technique was performed. It is well-known that the AA2024-T3 alloy has a heterogeneous structure with diverse intermetallics, responsible of the strengthening of the alloy matrix. However, these particles make the alloy susceptible to pitting corrosion when in contact with chloride-containing environments. The S phase particles (Al₂CuMg) are of special interest because they

represent over 70% of the total^{4,5}. The complex behavior of the S phase has been already discussed⁵; initially it is anodic with respect to the Al matrix due to the presence of magnesium. As immersion time progresses, Mg dealloying takes place and the particles becomes cathodic, due to Cu enrichment, causing dissolution of the surrounding Al matrix⁶. Figure 3A corroborates this mechanism: as can be seen the Al matrix undergoes an intense pitting attack. Nevertheless, when Mg²⁺ ions are present in the solution, there is no evidence of matrix attack at the same immersion period, that is to say, the S phase is still anodic (see figure 3B). This different behavior can be explained based on the EDX spectra shown in figure 3C. As it was stated before, the S phase in presence of chloride ions undergoes a progressive Mg dealloying and the consequent matrix attack. In the corresponding EDX spectra, the Mg peak has virtually disappeared. However, in the presence of Mg²⁺ ions, a high Mg peak intensity is observed, which indicates that the Mg dealloying was delayed.

Thus, it seems that the role of Mg^{2+} ions in aggressive electrolytes is focused on hindering the Mg dealloying process and, thus, the subsequent Al matrix attack.



Figure 3. SEM images of S phase after 15 minutes immersion in 10mM NaCl solution (A), or in 5mM $MgCl_2$ solution (B), 10.000x. The corresponding EDX spectra obtained from the S phase remnants.

Acknowledgements

This work has been supported by the Regional Program of Xunta de Galicia 10TMT303008PR.

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