

Effect of Intermetallics on the Corrosion of Al 2024-T3 Alloy in Solutions with Different Chloride Concentration

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Abstract. Al 2024-T3 is an important alloy very prone to localized corrosion. In this investigation the effect of chloride concentration on the corrosion resistance of the Al 2024-T3 alloy has been studied, focusing on the dissolution of the intermetallics (IMCs). Sodium chloride solutions of two concentrations, 0.6 M and 0.01mM, were used as test electrolytes. During the investigation selected regions of polished samples had their IMCs analyzed by Scanning Electron Microscopy (SEM) and X-ray Energy Analysis (EDX) prior and after different immersion times in the two test electrolytes. The results showed that even in the lowest chloride concentration the electrolyte was highly corrosive to the Al-Cu-Mg IMCs leading to their partial dissolution and to the attack of the surrounding matrix after only one hour of immersion. On the other hand, the corrosion behavior of the Al-Cu-Mn-Fe IMCs was random, and no correlation could be established between corrosive attack and chloride concentration or time of immersion for this type of particle. Atomic Force Microscopy (AFM) analyses have indicated a stronger dissolution of the matrix in the more concentrated electrolyte. This seems to lead to a milder attack of the IMCs in this solution when compared to the less concentrated one, as indicated in the SEM images.

1. Introduction

The Al 2024-T3 alloy is largely used in the aircraft industry due to its good mechanical properties resulting from the addition of alloying elements, mainly Cu and Mg. By controlled aging, these elements form small precipitates finely dispersed and coherent with the matrix improving the mechanical properties [1,2-5]. However, larger intermetallics (IMCs) are also formed during alloy solidification, which potentials differ from the matrix [2,6-9], originating local cells and leading to localized corrosion problems [6,10]. The two main types of coarse IMCs found in the Al 2024-T3 alloy are Al-Cu-Mg and Al-Cu-Mn-Fe, and their corrosion behavior has been largely investigated in literature [1,2,7,11-15].

There is general agreement that in chloride containing environments Al alloys rapidly corrodes. For Al 2024-T3 the corrosive attack is particularly severe on the Al-Cu-Mg IMCs, also denominated S phases. Most works agree that this phase is initially anodic to the matrix, but due to selective dissolution of Al and Mg, a porous and Cu-rich remnant is left behind, which is cathodic to the matrix and may lead to the corrosive attack of the surrounding matrix [7]. The Al-Cu-Fe-Mn IMCs, on the other hand, are usually considered as cathodic to the matrix. They are also more stable, and are reported to have less harmful effect on the Al 2024-T3 alloy corrosion resistance than the Al-Cu-Mg ones. Although it is generally accepted that the localized corrosion caused by the IMCs is the starting point for other types of corrosion in high resistance Al alloys [1,7], their role on the corrosion initiation is not yet well established. This is mainly due to their small size besides their chemical and microstructural complexity and the dependence of reactivity on the environment [8], moreover in-situ techniques are difficult to employ in the monitoring of corrosion phenomena.

In this study, the preliminary results obtained for the corrosion behavior of the Al 2024-T3 alloy in two electrolytes with different chloride concentrations are presented. The studies were performed using SEM/EDS characterization and AFM imaging.

Materials and Methods

The chemical composition of the Al 2024-T3 alloy used in this study, provided by Alcoa, is shown in Table 1.

Table 1. Chemical composition of the Al 2024-T3 alloy

Element	Al	Cu	Mg	Mn	Fe	Si	Zn	Ti
wt. %	93.3	4.86	0.59	0.7	0.28	0.19	0.26	0.1

The samples were prepared by grinding with silicon carbide paper and then polishing with diamond paste up to 1 μm finishing. After preparation, the surface was observed by Scanning Electron Microscopy (SEM) and analyzed by X-ray energy dispersive spectroscopy (EDX). Subsequently, the samples were immersed in either of two sodium chloride solutions, 0.6 mol/L or 0.01 mol/L, during periods of 1, 2 and 5 hours. After immersion, EDX and SEM were once again used to analyze the same region, and the surface morphology was evaluated by AFM (atomic force microscopy).

The SEM/EDX analyses were carried out with a Phillips model XL 30 microscope. The AFM analysis was performed with a NanoScope IIIA (Digital Instruments).

Results and Discussion

Surface characterization of the Al 2024-T3 alloy

In accordance with the literature, SEM/EDX analyse of all samples investigated showed two main types of coarse IMCs: Al-Cu-Mg and Al-Cu-Mn-Fe-(Si) [12,16]. The former presents a round shape with the biggest ones presenting diameters around 5 μm , whereas the Al-Cu-Mn-Fe IMCs present various sizes, often above 5 μm , with irregular morphology. Figure 1 shows a representative distribution of the IMCs in the Al alloy used in this study. Small Al-Cu-Mg IMCs [9] with sizes lower than 1 μm are also shown. It is also seen that IMCs can be either grouped or isolated [6,11].

Evolution of the IMCs morphology and chemical composition as a function of immersion time in sodium chloride solutions of different concentrations

SEM and EDX were employed to evaluate the morphology of both types of IMCs prior and after 1 and 2 hours of immersion in the 0.6 M and 0.01 M sodium chloride solutions. The overall results showed that the attack on S phase IMCs is faster than on Al-Cu-Mn-Fe ones, independently on the sodium chloride concentration.

Figure 2 shows micrographs of the Al 2024-T3 alloy after 1 hour of immersion in 0.6 M and 0.01 M sodium chloride. It is clearly shown that the attack of the Al-Cu-Mg IMCs and of the matrix surrounding them occurred during the first hour of immersion. On the other hand, for this period of immersion, the Al-Cu-Mn-Fe IMCs showed no signs of corrosive attack in either of the two solutions used. Interestingly, S phase IMCs seem more heavily attacked on the more dilute solution (compare Figures 2(c) and 2(d)). Moreover, comparing Figure 2(c) with Figure 1(b), which represents the same region, a moderate corrosive attack of the Al matrix near the corroded IMCs seems to be take place. The effect of Al-Cu-Mg IMCs on the corrosion behavior of the Al 2024-T3 has already been investigated in solutions of various chloride concentrations [5,17]. Pitting initiation is usually associated to the galvanic effect due to the selective dissolution of Al and Mg in

these precipitates. Indeed, analyses performed of the S phase precipitates presented in Figures 2(c) and (d) have shown a strong Cu enrichment.

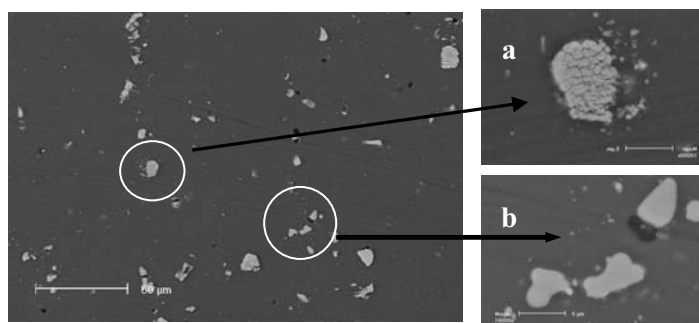


Figure 1 Micrographs of as-polished Al 2024-T3 alloy: (a) Al-Cu-Mn-Fe IMC and (b) Al-Cu-Mg IMCs.

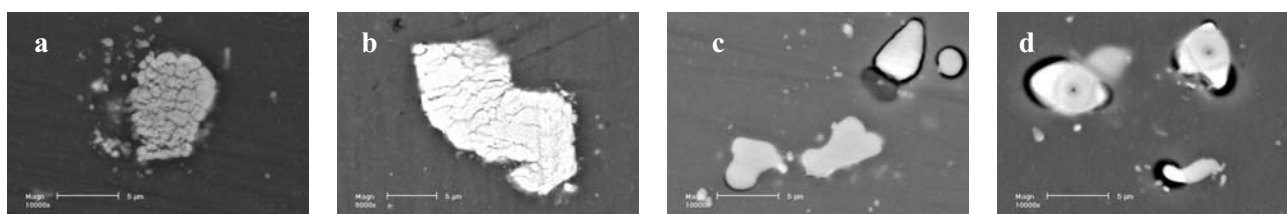


Figure 2 Micrographs showing IMCs on Al 2024-T3 surface after 1 hour of immersion in sodium chloride solution: (a) and (c) 0.6 M; (b) and (d) 0.01 M.

The corrosion behavior of the Al-Cu-Mn-Fe IMCs did not show any clear dependence either on immersion time or on NaCl concentration. Indeed the corrosion responses of these IMCs were very irreproducible. Previous studies carried out in our laboratory in 0.6 M NaCl showed that the matrix surrounding them was only attacked for immersion periods longer than 5 hours. For lower test periods there was only indication of selective dissolution of the IMC, as shown in Figure 3.

Figure 4 shows Al-Cu-Mn-Fe IMCs, which suffered significant corrosive attack after 2 hours of immersion in 0.01 M or 0.6 M NaCl solutions. It is clearly shown that after immersion in the 0.01 M NaCl solution, the IMC is more heavily attacked, presenting a powdery aspect mainly in the areas near to its borders. This could result from the deposition of corrosion products on the IMCs. EDX analysis on the IMCs prior to and after immersion showed the peak corresponding to oxygen only on the samples that had been previously immersed indicating the presence of oxides. One possible explanation for the stronger aggressiveness of the less concentrated solution towards the IMCs would be that in this condition the Al oxide layer on the matrix would be more stable. This would concentrate the corrosive attack within the IMCs, which have a more heterogeneous microstructure.

It must be emphasized that in some of the samples SEM/EDX analyses have shown no sign of corrosive attack in both types of IMCs, even after five hours of test. This was verified for the two concentration of chlorides investigated, and has been explained, for the Al-Cu-Mg IMCs, as resulting from the presence of a protective surface film, which, would protect them from corrosive attack until its removal [8,12,17].

AFM analysis of Al 2024-T3 surface after immersion in sodium chloride solutions

AFM topography analysis of Al 2024-T3 polished samples showed that the IMCs protrude from the surface. One of these IMCs had approximately 2.5 µm height after 1 hour immersion in 0.01 M NaCl solution, which was reduced to approximately 2 µm after 2h of test. Another sample tested in the more concentrated solution showed a height reduction from 1.4 µm to 0.9 µm during the same

time span. These results confirm the selective corrosive attack or dissolution within some of the IMCs, which had already been detected by the SEM images.

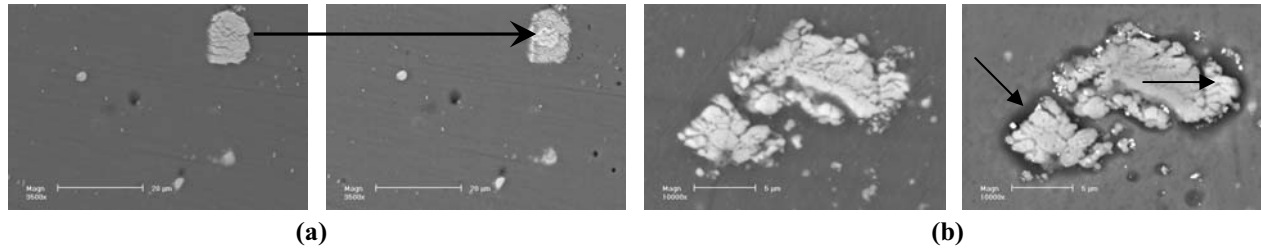


Figure 3 Micrographs of Al-Cu-Mn-Fe IMCs: (a) prior and after 1 hour of immersion in 0.6 M NaCl solution showing selective dissolution in the IMC and (b) prior to and after 5 hours of immersion. Arrows point towards the attacked regions of the IMCs.

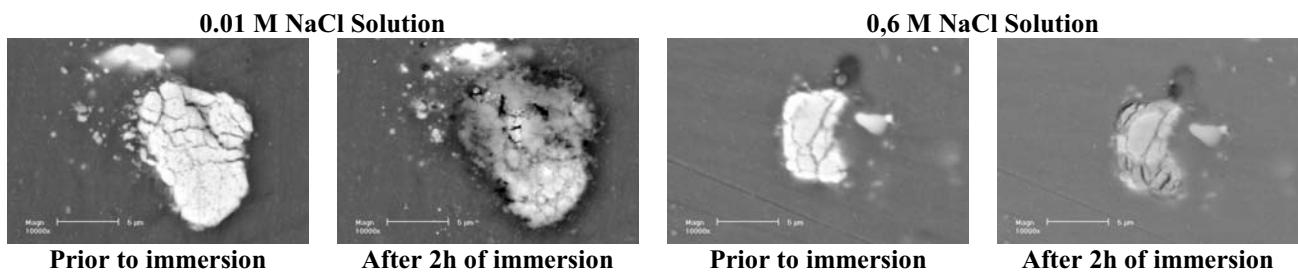


Figure 4 Micrographs of Al-Cu-Mn-Fe IMC prior and after 2 hours in 0.01 and 0.6M NaCl solution.

On the samples immersed in the 0.6 M NaCl solution a large number of small particles were found on the Al alloy surface after 2 hours of immersion. This could result from the generalized attack of the matrix, and corroborates with the proposed mechanism to explain the stronger susceptibility of the IMCs to corrosive attack in the most dilute chloride solution. Figure 5 shows AFM images obtained for samples that were immersed for 2 hours in the electrolytes used. The images indicate that the dissolution of the Al-Cu-Mg IMC had already started in either of the solutions, and the increased corrosive attack of the matrix in the more concentrated solution.

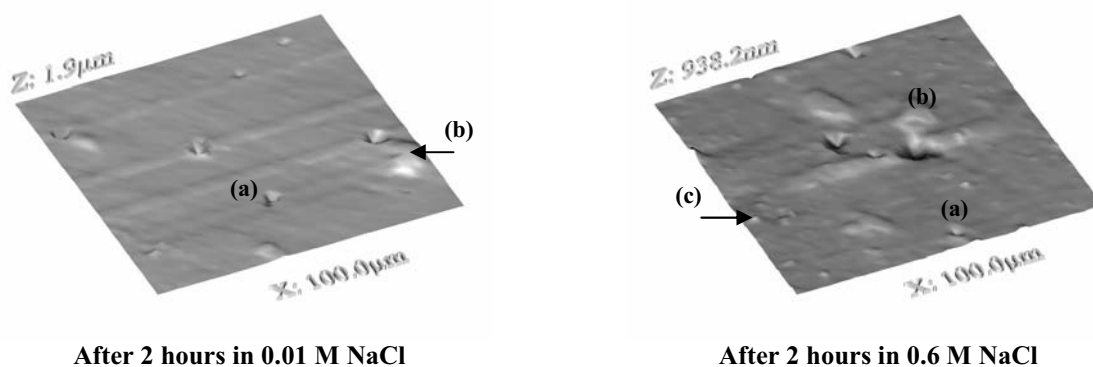


Figure 5 Topographic images obtained by AFM of Al 2024-T3 after immersion in sodium chloride solutions: (a) pits are due to corrosive attack of Al-Cu-Mg IMCs; (b) Al-Cu-Mn-Fe IMCs as protrusions on the surface; (c) small precipitates that emerged on the surface with immersion time.

Conclusions

The results showed that the Al-Cu-Mg IMCs present in the Al 2024-T3 alloy is rapidly attacked in solutions of various sodium chloride concentrations, such as the ones used in this study, specifically 0.01 M and 0.6 M. In both solutions, corrosive attack of these IMCs and selective dissolution was indicated by SEM or AFM analysis after only 1 hour of immersion. The Al-Cu-Mn-Fe IMCs, on

the other hand, showed an erratic behavior with some of these being intact after comparatively long periods (5 h) of immersion, whereas in others, visible signs of corrosion and selective dissolution were found after no more than 1 hour of test. The unpredictable behavior associated to this last type of IMCs points to the need of further investigation on the effect on the corrosion properties of the Al 2024-T3.

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