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Study of the effect of cerium nitrate on AA2024-T3 by means of electrochemical micro-cell technique

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ABSTRACT

This work evaluates the effect of cerium nitrate as corrosion inhibitor for AA2024-T3 in the view of its introduction in sol-gel coatings able to provide self-healing ability. Since it is well established that deposition of Ce species is activated by the local pH increase, the objective of this paper is to investigate the behavior of AA2024-T3 (open circuit potential and polarization curves) in the presence of Ce species in aggressive solutions by means of a local technique, the electrochemical micro-cell. This technique enables the investigation of small areas with resolution in the micrometer range by the use of glass capillaries to define the working electrode area.

The micro-cell results clearly displayed that the entire AA2024-T3 area exposed to the ceriumcontaining electrolyte was involved in the cerium precipitation mechanism. The heterogeneous electrochemical behavior of the microstructure is minimized by the formation of a cerium-containing layer able to protect the metal substrate.

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1. Introduction

The heterogeneous microstructure of AA2024-T3 aluminum alloy strongly affects its corrosion behavior [1–5]. Different kinds of coarse intermetallic particles have been identified in AA2024-T3 [6–8]. Buchheit reported a compilation of corrosion potentials for aluminum-based intermetallic particles found in the literature [9]. Corrosion potentials for intermetallic particles containing Al-Cu-Mg are more negative than those detected for intermetallic particles containing Al-Cu-Fe-Mn. As for AA2024-T3 aluminum alloy, Buchheit et al. [10] further highlighted that Al-Cu-Mg based intermetallic particles are the most numerous category while the second largest type is rich in Al-Cu-Fe-Mn. It has been found that immediately after immersion in a chloride solution, Al-Cu-Mg-based intermetallic particles interact as anodic sites with the aluminum matrix. However, magnesium and aluminum dissolution promotes the formation of Mg-Al-depleted intermetallic particles which can act cathodically for longer immersion times. Otherwise, Al-Cu-Fe-Mn intermetallic particles constantly interact as cathodes with the aluminum matrix [11-13]. The electrochemical behavior of second phase particles is affected by the pH solution and it can become very complex [14]. Therefore, the study of the electrochemical behavior of aluminum alloys is not easy and

can take into account several critical aspects. Boag et al. [15] investigated the local electrochemical behavior of AA2024-T3 by coupling SEM and EDXS analyses, which were used for mapping the alloy surface at different immersion times. It has been found that intermetallic particles, anodic and cathodic with respect to the matrix, play an important role in the corrosion behavior of the alloy but they were not able to quantify their influence. Battocchi et al. [16] used the scanning vibrating electrode technique (SVET) to measure the local current distribution of a wire beam electrode (WEB) made of AA2024-T3 wires. It has been found that the local surface conditions affected the heterogeneous electrochemical behavior of the alloy. Seegmiller and Buttry [17] used the scanning electrochemical microscopy (SECM) to investigate the cathodic activity at AA2024-T3 surfaces which turned out more intense on the intermetallic particles present in the microstructure rather than on the aluminum matrix.

In this view, the electrochemical micro-cell technique can be usefully employed for the evaluation of the micro-electrochemical behavior of metal microstructures [18]. The electrochemical microcell technique was initially employed by Suter et al. [19–21] to study the influence of sulfide inclusions on pitting initiation in stainless steels. Suter and Alkire [22], for the first time, employed the micro-cell technique to evaluate the electrochemical behavior of AA2024-T3 in the micrometer range. It has been found that the onset of pitting corrosion depends on the intermetallic particles category. In the case of Al–Cu–Mg-based intermetallic particles, it was observed that a fast magnesium and aluminum dissolution



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preferentially starts at the edge rather than at the center of intermetallic particles. In case of longer immersion time, the Al–Cu–Mg intermetallic particle type can become cathodic with respect to the surrounding matrix. On the other hand, the preferential dissolution of the matrix was mainly detected at the edge of Al–Cu–Fe–Mnbased intermetallic particles due to the galvanic coupling. The micro-cell technique was also employed for the study of the microelectrochemical behavior of AA7075 aluminum alloy [23–25]. The interaction of cathodic intermetallic particles (Al₇Cu₂Fe) with the matrix was fully investigated [26]. Al₇Cu₂Fe-based intermetallic particles promote the dissolution of the surrounding matrix inducing the formation of trenching corrosion morphologies. Furthermore, it was found that Mg₂Si intermetallic particles are anodic with respect to the matrix [27] and they represent the preferential site for the pitting corrosion initiation.

Salts of rare-earth elements are able to improve the corrosion behavior of aluminum alloys [28-30]. Hinton et al. [31-33] proved that rare-earths, and particularly cerium, inhibit redox reactions occurring on aluminum alloys. It was highlighted that the improvement of the corrosion resistance is due to the precipitation of cerium compounds on cathodic regions thus promoting the inhibition of reduction reactions [34]. Thanks to the first studies on the mechanism of cerium compounds precipitation, it was assumed that the process starts on regions where the pH solution tends to be increased by reduction reactions which produce chemical conditions favorable to cerium precipitation. It was hypothesized that the process continues in the surrounding regions via island growth involving small active regions which have not been covered yet [35]. Yasakau et al. [36] proved that, in case of the AA2024-T3 aluminum alloy, cerium precipitation preferentially occurs on Al-Cu-Mg-based intermetallic particles modified by the local magnesium and aluminum dissolution which leads to the overall copper-enrichment of the intermetallic particles. Despite the fact that many studies have focused on the comprehension of cerium precipitation mechanisms, there are some aspects which still need clarification such as the precipitation of cerium compounds on the matrix. In this work, the electrochemical micro-cell approach was used to evaluate the influence of the AA2024-T3 microstructure on the corrosion inhibition provided by cerium nitrate.

2. Materials and experimental procedure

2.1. Materials

AA2024-T3 samples were ground using SiC paper and subsequently polished using 6 and 1 μ m diamond suspensions. Ethanol was used instead of water in order to avoid or reduce the fast dissolution of the magnesium present on aluminum surfaces, especially as the constituent element of Al–Cu–Mg intermetallic particles.

2.2. Micro-electrochemical investigations

The micro-electrochemical investigation was carried out by means of the micro-cell technique. The micro-cell apparatus basically consists of a glass microcapillary embedded in a micro-cell which is mounted on the revolving nosepiece of an optical microscope. This setup enables to point the measurements towards the region desired by observing the surface with the optical microscope. The sealing at the glass capillary tip is ensured by a silicone layer which prevents to avoid solution leakage [18]. A standard three electrode setup was employed for micro-electrochemical measurements where the working electrode corresponded to the exposed area defined by the diameter size of the glass micro capillary.

In this work, micro capillaries of 50 µm size were employed. The counter electrode was a 1.5 mm platinum wire while an Ag/AgCl electrode was used as reference. The micro-electrochemical cell employed in this work is of the form reported by Suter [18,19]. All electrodes were connected to a potentiostat/galvanostat (IPS - Elektroniklabor Peter Schrems) able to measure currents in the range of fA. Three different kinds of surface regions were studied by means of micro-cell technique: regions where intermetallic particles are not visible (indicated in the paper as matrix), regions containing a high amount of Al-Cu-Mg-based intermetallic particles and regions containing a high number of Al-Cu-Fe-Mnbased intermetallic particles. Open circuit potential measurements (OCPs) were performed for 5 min in order to evaluate the stability of the region identified by the micro capillary mouth. Potentiodynamic polarization curves were then acquired on the same area exposed during OCP measurements. A scan rate of 1 mV s⁻¹ was used to perform polarization curves. Anodic and cathodic branches were acquired separately. Anodic branches were detected starting near the OCP. Cathodic branches were rather acquired starting from a potential slightly more negative than the open circuit potential just measured. This procedure was adopted in order to prevent a possible anodic polarization which could have affected the cathodic behavior of the aluminum alloy surface covered by cerium compounds. All the micro-electrochemical measurements were performed in a 0.05 M NaCl aqueous solution

In order to evaluate the effect of cerium on the corrosion behavior of the AA2024-T3 microstructure, OCP and polarization tests were performed on AA2024-T3 samples before and after immersion in a 0.05 M NaCl solution containing $5 \, g \, L^{-1} \, Ce(NO_3)_3 \cdot GH_2 O$. Polished samples were immersed for 12 h in the cerium solution in order to allow cerium precipitation. In order to obtain reliable results, for each region of interest and for each surface condition (before and after interaction with cerium), more than 20 of both OCP measurements and polarization curves were carried out. Following an approach based on the employment of localized techniques, it is very important to acquire a reasonable number of measurements able to validate the experimental results.

2.3. Scanning electron microscopy

Scanning electron microscopy (SEM) observations were combined with electrochemical measurements. The combination of the two techniques allowed to associate the electrochemical results with the surface morphologies observed with SEM. In order to enable the characterization of the same area of the sample before and after immersion in the cerium-containing solution, the investigated areas were marked with a grid of indentations prepared using a Vickers micro-indenter (Struers Micro-Indenter). Square areas of 100 μ m × 100 μ m size were marked. This procedure enables to perform easily both SEM and micro-cell characterizations on the same sample area. A Carl Zeiss EVO 40XVP microscope equipped with the INCA ENERGY 250 microanalysis apparatus was used.

3. Results and discussion

3.1. AA2024-T3 microstructure

Fig. 1 shows the surface morphology of AA2024-T3 after polishing detected by means of scanning electron microscopy. The image was acquired by collecting the back-scattered electron signal emitted by the metal surface. From this picture, it is possible to recognize the heterogeneous microstructure of the alloy. The dark area corresponds to the aluminum matrix while the brighter regions are

Table 1	
EDXS chemical composition (wt%) of the regions marked in Fig. 1.	

	Al (wt%)	Cu (wt%)	Mg (wt%)	Fe (wt%)	Mn (wt%)	Si (wt%)
Matrix (Spectrum 1)	93.84 ± 0.4	4.30 ± 0.3	1.86 ± 0.1	-	-	-
Mg-rich INT (Spectrum 2)	88.40 ± 0.4	8.09 ± 0.4	3.52 ± 0.1	-	-	-
Fe-rich INT (Spectrum 3)	65.54 ± 0.5	7.79 ± 0.3	-	13.06 ± 0.3	9.34 ± 0.2	4.27 ± 0.4

associated to the second phase particles. As explained in Section 2. in this work, three regions were considered as interesting areas for the evaluation of cerium precipitation mechanisms: regions rich in Al-Cu-Mg intermetallic particles (from now on called Mgrich), regions rich in Al-Cu-Fe-Mn intermetallic particles (from now on called Fe-rich) and regions with a very small amount of intermetallic particles (from now on called matrix). In Table 1 the chemical composition of the regions identified by the three boxes in Fig. 1 is reported: the matrix, the iron-rich intermetallic region and the magnesium-rich intermetallic region. EDXS analysis (Table 1) performed on the matrix area (Spectrum 1) evidences a chemical composition in accordance with commercial AA2024-T3 aluminum alloys [1]. Spectrum 2 can be associated to an intermetallic particle rich in Al-Cu-Mg because the amount of magnesium and copper is higher than the one detected in the matrix (Spectrum 1). In Spectrum 3, in addition to copper and aluminum signals, iron, manganese, and silicon were detected. This chemical composition can be associated to the Al-Cu-Fe-Mn intermetallic particle type. It has been further seen and confirmed by a deeper investigation that intermetallic particles rich in iron are usually larger than those rich in magnesium as found by Buchheit et al. [10]. While the maximum size of the magnesium-rich type is in the range of a few micrometers, the size of the iron-rich type can vary in a large range from a few micrometers up to 20 µm. Since in this work capillaries with an average diameter of 50 μ m were used, the area directly exposed to the electrolyte necessarily includes both intermetallic particles and a fraction of matrix. This aspect has to be taken into account for the explanation of the results. It is also important to point out that it was easier to perform micro-electrochemical measurements on regions containing iron-rich intermetallic particles than on regions containing magnesium-rich intermetallic particles. Indeed, Al-Cu-Mg-based intermetallic particles are more reactive than those rich in iron because immediately after immersion, magnesium dissolution strongly affects the electrochemical behavior. This aspect will be discussed in detail in Section 3.3.

3.2. Open circuit potential before immersion in cerium nitrate

Fig. 2 shows the open circuit potential in 0.05 M NaCl for polished AA2024-T3 samples measured on the three areas of interest defined in Section 2: the matrix region (solid line), the region containing iron-rich intermetallic particles (long-dashed line) and the region containing magnesium-rich intermetallic particles (dashdotted line). The matrix and iron-rich intermetallic regions behave in a similar way. In the case of the matrix (solid line), immediately after immersion OCP is -500 mV vs. Ag/AgCl and after 300 s the value is very close to the one detected at the beginning. However, some spikes were detected during the OCP measurement on the matrix. The first small OCP variation can be identified after 50 s, while after 130 s, the OCP suddenly starts to decrease to -600 mV vs. Ag/AgCl. In the range between 130 and 200 s, the OCP for the matrix region appears noisy suggesting that corrosion attacks are taking place. This evidence can likely be associated to a localized corrosion attack which is typical of AA2024-T3 aluminum alloys [9]. Immediately after immersion. OCP for the region containing ironrich intermetallic particles (long-dashed line) is equal to -510 mV vs. Ag/AgCl and tends to continuously increase. It reaches -360 mV vs. Ag/AgCl after 300 s immersion. The OCP shift towards more positive values might be related to the activation of reduction reactions at the intermetallic particle surface which behaves cathodically with respect to the matrix [37]. The OCP trend for the region containing magnesium-rich intermetallic particles (dash-dotted line) is not as constant as in the previously discussed case. Immediately after immersion, magnesium strongly affects the OCP which is -640 mV vs. Ag/AgCl. For longer immersion time, the OCP shifts from very negative values (the minimum value is in the range of -1000 mV vs. Ag/AgCl) to values typical of the aluminum matrix (close to -500 mV vs. Ag/AgCl). For magnesium-rich intermetallic regions, the unstable OCP trend can be due to the high electrochemical activity of magnesium which quickly dissolves during the first period of immersion. In many cases (not here represented), immediately after immersion, the OCP of magnesium-rich intermetallic regions was very active (down to -1100 mV vs. Ag/AgCl) shifting to



Fig. 1. SEM morphology of the polished AA2024-T3 surface.



Fig. 2. Open circuit potential for the AA2024-T3 microstructure in 0.05 M NaCl acquired using a glass micro-capillary of 50 μm size.



Fig. 3. Anodic (a) and cathodic (b) polarization curves for the AA2024-T3 microstructure in 0.05 M NaCl acquired using a glass micro-capillary of 50 μ m.

values typical of the matrix (close to -500 mV vs. Ag–AgCl) before the end of the measurement (300 s). In these cases, the results of potentiodynamic polarization measurements, which will be discussed in Section 3.3 (Results and Discussion), were very similar to those obtained on the matrix regions. In those cases, the magnesium content was totally dissolved during free immersion and the area which underwent polarization was probably consisting of both the matrix and the intermetallic particles depleted in magnesium and rich in copper. This evidence was one of the most critical points to be considered in the experimental approach for the evaluation of the micro-electrochemical behavior of AA2024-T3. From this point of view, the polishing procedure has had an important role, because, as explained in Section 2, it was very important to prevent magnesium dissolution during sample preparation.

3.3. Potentiodynamic polarization curves before immersion in cerium nitrate

As explained in Section 2.2, the polished AA2024-T3 surface was electrochemically characterized by acquiring a large number of anodic and cathodic polarization curves. The results discussed in the paper are therefore representative of the overall measurements carried out. Table 2 reports the average and the standard deviation of corrosion and breakdown potentials for all the anodic polarizations carried out in 0.05 M NaCl. Fig. 3 shows anodic and cathodic potentiodynamic polarization curves in 0.05 M NaCl for polished AA2024-T3 on the three areas of interest: the matrix region (solid line), the region containing iron-rich intermetallic



Fig. 4. Corrosion morphology of a region containing a coarse Al-Cu-Fe-Mn intermetallic particle.

particles (long-dashed line) and the region containing magnesiumrich intermetallic particles (dash-dotted line). The potentiodynamic polarization curves were performed on the same area exposed to the electrolyte during OCP measurements. The anodic behavior shown in Fig. 3(a) evidences that the matrix and iron-rich intermetallic regions behave in a similar way. For iron-rich intermetallic regions, E_{corr} is more positive than that acquired for the matrix, confirming the trend evidenced by OCP measurements. For regions containing iron-rich intermetallic particles, icorr is around $1 \,\mu\text{A}\,\text{cm}^{-2}$ which is almost one order of magnitude higher than that evaluated for the matrix region. This result can be explained considering that in the region containing iron-rich intermetallic particles, a fraction of the area exposed to the electrolyte is made of matrix. Hence, aluminum matrix dissolution is promoted by the galvanic coupling with iron-rich intermetallic particles leading to higher corrosion rates. Fig. 4 shows the corrosion morphology of a region containing Al-Cu-Fe-Mn intermetallic particles. The image was acquired after the carrying out the anodic polarization. A deep corrosion attack can be seen in the aluminum matrix near the intermetallic particle boundary. This evidence is related to the higher corrosion current density detected for iron-rich intermetallic regions with respect to that identified for regions containing only the matrix. This behavior can also be associated to the different breakdown potentials exhibited by matrix and iron-rich intermetallic regions. The natural oxide layer grown on the interface between the matrix and the intermetallic particles tends to be weak. These are the points where the oxide can be dissolved by polarizing anodically the substrate. Corrosion of the matrix can be otherwise related to the presence of strengthening particles which can act as precursor sites for the onset of localized corrosion attacks. However, this aspect has not been considered in this paper because it will be a part of another work, in which a combination of different localized techniques has been considered. In Fig. 3(a), it is possible to observe that for the matrix, the passive region is wider than for iron rich intermetallic particles. The breakdown potential related to the localized corrosion attack can be identified at -290 mV and -330 mV vs. Ag/AgCl for the matrix and the iron-rich intermetallic regions, respectively. The anodic behavior of regions containing magnesium-rich intermetallic particles (Fig. 3(a)) is rather different compared to the anodic behavior of both the matrix and the iron-rich intermetallics regions. For magnesium-rich intermetallic regions, E_{corr} is more active than the ones of other regions. This evidence confirms OCP measurement results. Magnesium strongly influences the electrochemical behavior of every alloy and in the case of AA2024-T3, second phase

Table 2

Average and standard deviation of corrosion and breakdown potentials (both vs. (Ag/AgCI)/mV) calculated from anodic polarizations carried out in 0.05 M NaCl.

	$E_{\rm corr}~({\rm mV})$	Standard deviation (mV)	Breakdown potential (mV)	Standard deviation (mV)
Matrix	-437.1	34.4	-228.2	25.6
Mg-rich INT	-748.4	81.6	-564.6	59.2
Fe-rich INT	-323.7	21.6	-312.1	17.6

particles containing a high magnesium amount have a remarkable effect on *E*_{corr}. From Fig. 3(a), for magnesium-rich intermetallic regions, i_{corr} is about 20 μ A cm⁻² which is two orders of magnitude higher than for the matrix. The breakdown potential can be identified at -640 mV vs. Ag/AgCl which is very active with respect to those exhibited by the matrix and the iron-rich intermetallic particles. The magnesium effect on the electrochemical behavior of AA2024-T3 can also be evaluated in Fig. 3(b) where cathodic potentiodynamic polarization curves are reported. The matrix and the iron-rich intermetallic regions exhibit a similar cathodic behavior near $E_{\rm corr}$ where the oxygen reduction and the hydrogen evolution reactions take place. At much more negative potentials than $E_{\rm corr}$, cathodic reactions taking place on both matrix and ironrich intermetallic regions are strongly increased. The increase is most likely related to the water reduction reaction occurring at these potentials. The cathodic current densities exhibited by the magnesium-rich intermetallic regions are higher than those measured on the matrix. For magnesium-rich intermetallic regions, at a potential that is around -1000 mV vs. Ag/AgCl, the current densities are in the range of $400 \,\mu A \, \text{cm}^{-2}$ which are one order of magnitude higher than those measured for the matrix region. At these potentials, on regions rich in magnesium intermetallic particles, a strong bubble evolution, which can be likely related to an intense hydrogen reduction reaction, was observed [38]. At the end of the micro-electrochemical investigation carried out on bare AA2024-T3, it is possible to state that magnesium strongly affects the corrosion behavior of the alloy. Anodic and cathodic reactions are heavily dependent on the amount of magnesium contained in the region under investigation. In Section 3.4, the effect of cerium nitrate on the heterogeneous electrochemical behavior of AA2024-T3 aluminum alloy will be discussed.

3.4. Open circuit potential after immersion in cerium nitrate

Fig. 5 shows the open circuit potential for polished AA2024-T3 in 0.05 M NaCl measured after 12 h immersion in 0.05 M NaCl containing 5 g L^{-1} Ce(NO₃)₃·6H₂O. Measurements were performed on



Fig. 5. Open circuit potential for the AA2024-T3 microstructure in 0.05 M NaCl, after 12 h of immersion in cerium nitrate, acquired using a glass micro-capillary of 50 μ m size.

matrix regions (thick solid line), on regions containing iron-rich intermetallic particles (thick long-dashed line) and on regions containing magnesium-rich intermetallic particles (thick dash-dotted line). OCP measurements acquired before immersion in the solution containing cerium (see Fig. 2) are reported here as reference (thinner lines). By comparing OCP measurements before and after immersion in cerium solution, it is possible to point out that a remarkable modification of the electrochemical behavior can be observed for the entire surface. For the matrix, the iron-rich and the magnesium-rich intermetallic regions, OCP tends to be more positive than before immersion in cerium (thinner lines) and for all three regions, after 50s in 0.05 M NaCl, a steady state condition is reached and maintained until the end of the measurement suggesting that a cerium film has been deposited everywhere. Fig. 6 shows a detail of the AA2024-T3 surface modified by the cerium interaction. The figure shows the surface morphology of an iron-rich intermetallic region (with cathodic behavior) after 12 h of immersion in 0.05 M NaCl containing $5 g L^{-1} Ce(NO_3)_3 GH_2O$. From the picture, it is possible to recognize the presence of a very thin cerium film on the iron-rich intermetallic particle only because a film crack is visible. On the surrounding matrix, it is not possible to recognize the cerium film. This does not mean that the film is not present but that the film is only too thin to be observed. SEM-EDXS analyses performed on the region considered in Fig. 6 are not able to clearly identify the cerium signal because the penetration depth of the electron beam into the specimen is in the range of micrometers while the film thickness is probably in the range of a few nanometers. Hence, the contribution of the thin cerium film on the X-ray generation is not enough to guarantee a clear cerium signal. As well known in the literature [35], cerium precipitation occurs on regions where cathodic reactions take place. However, as shown in Fig. 7, cerium compounds were also observed not only on intermetallic particles with a cathodic behavior (Fig. 6) but also on intermetallic particles with anodic behavior (Al-Cu-Mgbased) as intense precipitates, already determined by Yasakau et al. [36]. Table 3 shows the EDXS micro-chemical composition of the region containing the magnesium-rich intermetallic particles which is indicated with the arrows in Fig. 7(a) and (b). Before



Fig. 6. Surface morphology of a coarse Al–Cu–Fe–Mn intermetallic particle after 12 h immersion in cerium nitrate.

Table 3		
EDXS chemical composition (v	t%) of the marked region indicated by the circle in Fig. 7 acquired before (a) and after (b) immersion in cerium r	nitrate.

	Al (wt%)	Cu (wt%)	Mg (wt%)	Ce (wt%)	O (wt%)
Before immersion After immersion	$\begin{array}{c} 64.78\pm0.5\\ 4.81\pm0.1\end{array}$	$\begin{array}{c} 26.39 \pm 0.4 \\ 2.12 \pm 0.2 \end{array}$	7.46 ± 0.2	$-$ 55.45 \pm 0.4	$\begin{array}{c} 1.11 \pm 0.3 \\ 37.26 \pm 0.4 \end{array}$

immersion (Fig. 7(a)), a high amount of magnesium was detected (7.46 wt%), which was not detected on the same region after immersion (Fig. 7(b)). On the other hand, an intense signal of cerium and oxygen was detected suggesting that a heavy cerium precipitation occurred in this region during immersion in cerium-containing solution. Since after immersion the aluminum signal drastically decreases, the precipitate is probably thick enough to shield the metal substrate. EDXS analysis does not allow to acquire signals deeper than a couple of micrometers (depending on the material under investigation), and the low aluminum signal acquired is a consequence of this limitation.

In the AA2024-T3 aluminum alloy, immediately after immersion, Al–Cu–Mg intermetallic particles behave anodically [39] but they can behave cathodically after magnesium dissolution. From Fig. 7(b), it is possible to recognize that on the marked region a wide precipitation occurred covering the magnesium-rich intermetallic particles. The dark matrix region appears smoother than the bright magnesium-rich intermetallic particles, suggesting that the precipitation which occurred on the matrix was not as strong as on magnesium-rich intermetallic particles [36]. Eckermann et al. [40] studied the micro-electrochemical reactivity of intermetallic particles present in another group of aluminum alloys mainly



Fig. 7. Surface morphology of an AA2024-T3 marked region acquired before (a) and after (b) immersion in cerium nitrate.

containing Al-Mg-Si. It has been found that an increasing of solution pH can be identified on MgSi intermetallic particles which should have an anodic behavior with respect to the matrix. Two different hypotheses have been formulated to explain that evidence. The first explanation is related to the development on MgSi particles of a strong hydrogen reduction associated to a fast magnesium dissolution [41]. The second mechanism takes its stand on the hypothesis that after magnesium dissolution, MgSi particles can change their behavior from anodic to cathodic. On modified MgSi particles, reduction reactions can occur producing the local increase in pH. A similar explanation can be given for the microelectrochemical behavior of Al-Cu-Mg particles embedded in the AA2024-T3 microstructure investigated in the present work. The cerium deposition mechanism can be therefore related to the fast magnesium dissolution which should be able to supply electrons for cathodic reactions occurring very close to the anodic region. This first mechanism considers that magnesium dissolution and cathodic reactions occur together on intermetallic particles rich in magnesium which are immediately covered by cerium precipitation. Otherwise, a second cerium precipitation mechanism can be based on a slower precipitation kinetic. Measurements shown in Fig. 2 evidence that the OCP for magnesium-rich intermetallic particles can shift from very negative potentials to potentials typical of the matrix in a very limited length of time. As already discussed, it is possible to suppose that a main part of the total amount of magnesium completely dissolves before cerium precipitation guickly occurs. If this happens, intermetallic particles are depleted in magnesium and are rich in copper and aluminum. Hence, it is possible that cerium precipitation occurs on the magnesium-depleted intermetallic particles which in the meantime might behave similar to a binary intermetallic particle rich in copper and aluminum. Binary Al-Cu intermetallic particle is more positive than both the ternary Al-Cu-Mg and the Al-Cu-Fe-Mn types [9]. It is reported [9] that in sodium chloride, the corrosion potential of the Al-Cu binary compound is -0.32 mV vs. SCE while that of the Al-Cu-Mg type is -0.92 mV vs. SCE. The difference in corrosion potentials might explain how a preferential cerium precipitation might occur on magnesium-depleted intermetallic particles where cathodic reactions directly occur promoting the increase of the local pH needed for cerium compounds precipitation. It is very difficult to prove what of the mechanism is more probable but a combination of the two routes may be a reasonable hypothesis.

Fig. 7(a) and (b) allows us to confirm that the preferential sites for cerium precipitation are those rich in magnesium [36]. However, since cerium precipitation occurred on the entire AA2024-T3 surface, the film growth can be explained by considering the islandgrowth mechanism proposed by Hughes et al. [35] for aluminum alloys. According to this mechanism, the island-growth considers the microstructure of metal substrates as a collection of microanodes and micro-cathodes where an increasing in the local pH, necessary for cerium precipitation, can occur. Cerium precipitation is then limited when the entire surface is covered by the spontaneous film deposition.

3.5. Potentiodynamic polarization curves after immersion in cerium nitrate

Fig. 8 shows potentiodynamic polarization curves in 0.05 M NaCl after immersion in the solution containing cerium for the three

Table 4

Average and standard deviation of corrosion and breakdown potentials (both vs. (Ag/AgCl)/mV), after 12 h immersion in cerium nitrate solution, calculated from anodic polarizations carried out in 0.05 M NaCl.

	$E_{\rm corr} ({\rm mV})$	Standard deviation (mV)	Breakdown potential (mV)	Standard deviation (mV)
Matrix	-98.1	22.4	-34.3	23.2
Mg-rich INT	-322.5	42.4	+58.2	49.6
Fe-rich INT	-224.6	28.8	-84.2	12.8

areas of interest: the matrix region (solid line), the region containing iron-rich intermetallic particles (long-dashed line) and the region containing magnesium-rich intermetallic particles (dashdotted line). Potentiodynamic polarization curves were performed on the same area exposed to the electrolyte during OCP measurements (see Fig. 5). Table 4 reports the average and the standard deviation of corrosion and breakdown potentials calculated from all the anodic polarizations carried out in 0.05 M NaCl, after 12 h immersion in cerium-containing solution. After cerium immersion, for all three regions, *E*_{corr} shifts towards more positive values confirming OCP results. In the case of the matrix region, $E_{\rm corr}$ shifts from -400 mV to -100 mV vs. Ag/AgCl provoking a ΔE_{corr} equal to 300 mV. For the region containing iron-rich intermetallic particles, E_{corr} shifts from -360 mV to -200 mV vs. Ag/AgCl while it changes from -800 mV to -300 mV vs. Ag/AgCl for the region rich in Al-Cu-Mg intermetallic particles. Regions containing magnesium-rich intermetallic particles exhibit the largest ΔE_{corr} . Due to the immersion in cerium solution, i_{corr} is also subjected to



Fig. 8. Anodic (a) and cathodic (b) polarization curves for the AA2024-T3 microstructure in 0.05 M NaCl, after 12 h of immersion in cerium nitrate, acquired using a glass micro-capillary of $50 \,\mu$ m.

a strong reduction. In the case of matrix regions, i_{corr} changes from $0.2 \,\mu\text{A}\,\text{cm}^{-2}$ (Fig. 3) to $0.03 \,\mu\text{A}\,\text{cm}^{-2}$ (Fig. 8). For the region containing iron-rich intermetallic particles, before immersion, i_{corr} is $2 \mu A \text{ cm}^{-2}$ while it is reduced to $0.03 \mu A \text{ cm}^{-2}$ after immersion. Regions containing magnesium-rich intermetallic particles evidence the largest Δi_{corr} : before immersion i_{corr} is 20 μ A cm⁻² while after immersion it decreases down to 0.06 μ A cm⁻². It is important to point out this evidence because regions containing magnesiumrich intermetallic particles, before immersion in a cerium solution, tend to corrode faster than both the matrix and the regions containing iron-rich intermetallic particles. After cerium precipitation, corrosion current densities measured on the entire surface are closer to a common value than before immersion. Moreover, areas containing magnesium-rich intermetallic particles display a very wide passive region (Fig. 8) which is larger than that exhibited by both the matrix and the iron-rich intermetallic regions. By considering Fig. 3(a), the anodic behavior of magnesium-rich intermetallics regions is considerably improved by the immersion in the cerium solution (Fig. 8(a)). After immersion in the cerium solution, the passive current densities are two orders of magnitude lower than those before immersion. The breakdown potential is around +50 mV vs. Ag/AgCl which is 100 mV and 150 mV more positive than for the matrix and the iron-rich intermetallic region, respectively. The effect of cerium precipitation can also be evaluated considering the cathodic behavior (Fig. 8(b)). Reduction reactions occurring on the entire substrate are strongly reduced by cerium precipitation. In particular, cathodic current densities measured on regions containing magnesium-rich intermetallic particles are strongly limited since they are reduced more than two orders of magnitude. The strong current reduction observed for the magnesium-rich intermetallic region can be related again to the high amount of cerium compounds precipitated on this region. However, the inhibition of cathodic reactions exhibited by the entire surface confirms that cerium precipitation involves all the microstructure. The electrochemical behavior of the three regions of interest is therefore more homogeneous than before immersion in the electrolyte containing cerium. After cerium precipitation, which clearly occurs on the entire exposed surface, both the anodic and the cathodic behaviors appear very similar for the three regions investigated. In agreement with a recent paper written by Birbilis et al. [42], ceriumcompounds are able to provide anodic and cathodic inhibitions. Birbilis, however, reported an increase in corrosion potential with the presence of cerium dibutyl phosphate only for S-phase intermetallic particles. A decrease in corrosion potential was detected for intermetallic particles with a cathodic behavior with respect to the aluminum matrix. This apparent disagreement is probably due to the different approaches used because, in the case of the approach followed by Birbilis, intermetallic compounds of thousands micrometers in diameter were synthesized and tested without the influence of the aluminum matrix which was instead considered by the experimental approach adopted in the present work.

Fig. 9 shows a region containing a large intermetallic particle with a very complex chemical composition. The three images ((a), (b) and (c)), were acquired after the anodic polarization carried out subsequently to the immersion in the solution containing 5 g L^{-1} cerium nitrate. Table 5 shows the average chemical composition



Fig. 9. Surface morphology of a mixed Al-Cu-Fe-Mn/Al-Cu-Mg intermetallic particle after the carrying out anodic polarization in 0.05 M NaCl. Before the measurement, the AA2024-T3 sample was hold for 12 h in cerium nitrate.

Table 5

EDXS chemical composition (wt%) of the intermetallic regions indicated in Fig. 9. The average composition of the entire intermetallic was acquired before the immersion in cerium nitrate while localized analyses were performed after the anodic polarization measurement.

	Average composition before immersion	Region 1 after immersion	Region 2 after immersion
Al (wt%)	70.62 ± 0.5	18.85 ± 0.5	52.33 ± 0.6
Cu (wt%)	10.38 ± 0.3	7.57 ± 0.6	8.77 ± 0.5
Mg (wt%)	2.23 ± 0.1	-	-
Fe (wt%)	6.71 ± 0.2	-	15.46 ± 0.4
Mn (wt%)	4.69 ± 0.2	-	10.97 ± 0.4
Si (wt%)	2.25 ± 0.1	-	-
Ce (wt%)	-	41.62 ± 0.8	1.29 ± 0.3
O (wt%)	3.11 ± 0.4	30.35 ± 0.8	7.12 ± 0.6

acquired on the whole intermetallic particle before immersion in the cerium-containing solution. In Table 5, the chemical compositions of Region 1 and Region 2 after immersion in cerium nitrate are also reported. As shown in Table 5, Mg, Al, Cu, Fe, Mn, and Si signals were detected in the average composition of the intermetallic particle before immersion in cerium. The latter three elements, with Cu and Al, form intermetallic particles with cathodic behavior [9] while intermetallic particle types containing Mg, Al, and Cu behave anodically with respect to the matrix. Hence, the intermetallic particle observed in Fig. 9 is probably made of second phase particles with different micro electrochemical behavior. The intermetallic particle is probably formed by the combination of a part rich in Al-Cu-Mg (Region 1) and another part containing Al-Cu-Fe-Mn (Region 2). In Fig. 9(a), the silicon mark produced by the contact between the capillary mouth and the AA2024-T3 surface defines the area exposed to the electrolyte during the measurement. It corresponds to a diameter in the range of 50 μ m as the size of the glass capillary. Fig. 9(c) shows the localized corrosion attack at the matrix near to the interface with the intermetallic particle (Region 2). The corrosion attack occurred in correspondence with a restricted edge. In the opposite part of the intermetallic particle (Region 1), no evidence of corrosion is observed (Fig. 9(b)). In Fig. 9(b), relevant to Region 1, it is also possible to recognize a strong cerium precipitation (see Table 5) which was most likely able to protect the metal substrate when the anodic polarization measurement was carried out. The chemical micro-analysis carried out on the intermetallic region represented in Fig. 9(c) exhibits a weak signal of cerium and oxygen while intense peaks of iron and manganese were detected. Then, the pitting corrosion of the matrix visible in Fig. 9(c), occurred in correspondence with the intermetallic particle interface rich in iron and manganese. The small amount of cerium detected and the morphology observed in Fig. 9(c) indicate that a very thin film covers this part of the intermetallic particle and the surrounding matrix. The same evidence was observed for the iron-rich intermetallic particle of Fig. 6. The corrosion attack identified at Region 2 is probably related to a limited protection provided by cerium compounds while the Region 1 is completely covered by a thick cerium precipitate. This aspect evidences one more time that on

intermetallic regions rich in iron and manganese, cerium precipitation is less intense than on regions rich in magnesium-intermetallic particles.

4. Conclusions

The electrochemical micro-cell technique has been employed for the micro-evaluation of the effect of cerium nitrate on the corrosion behavior of AA2024-T3 aluminum alloy. Magnesium-rich and iron-rich intermetallic particles have been considered as well as the matrix region. The corrosion behavior of AA2024-T3 samples after immersion for 12 h in the solution containing the cerium nitrate salt is significantly improved. The precipitation of thin cerium compounds covering the entire metal surface improves both the anodic and the cathodic behavior of the different analyzed regions. Hence, the electrochemical behavior of the considered aluminum alloy appears to be quite improved after the precipitation of cerium compounds on both the matrix and the areas containing intermetallic particles.

Cerium precipitation mechanism depends on the local pH values controlled by the cathodic reactions occurring on the whole metal surface for which the kinetics is affected by the specific cathodic activity of each considered region (matrix or intermetallic particles). In particular, regions containing high amounts of magnesium-rich intermetallic particles are very reactive. The cerium deposition mechanism can be therefore related to the fast magnesium dissolution which should be able to supply electrons for cathodic reactions occurring very close to the anodic region. This mechanism considers that magnesium dissolution and cathodic reactions occur together on intermetallics rich in magnesium which are immediately covered by cerium precipitation. Therefore, magnesium-rich intermetallic regions showed to be sites where a more intense cerium precipitation can occur. Due to the intense cerium precipitation, these areas become electrochemically more stable and the overall current flow related to Faradic processes involving the entire microstructure regions is strongly reduced.

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