



The repassivation response from single cycle anodic polarization: The case study of a sensitized Al-Mg alloy



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ABSTRACT

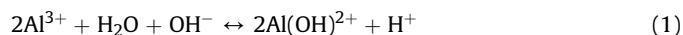
The repassivation behaviour of artificially aged 5083-H111 Al-Mg alloy in near neutral NaCl solutions was investigated by means of single cycle anodic polarization. Artificial aging was carried out at 150 °C during different times up to 360 h. The characterization of the microstructure and composition by XRD, SEM/EDS and metallographic analyses pointed out most favoured grain-boundary β (Al₃Mg₂) phase precipitation for 168 h of isothermal treatment time. Nitric acid mass loss test (NAMLT) and microhardness measurements indicated the highest degree of sensitization (DoS) and developed strength for 168 h as well. For all the aging conditions, the potential drop at high currents during the reverse scan of the cyclic polarization was detected at the pit transition potential E_{ptp} with similar but higher values than the corrosion potential of β phase ($E_{\text{corr}} \approx -900$ mV vs SCE). The associated current density i_{ptp} and the steepness of the potential drop increase as the amount and contiguity of β phase precipitates along grain boundaries. The onset and sustenance of metastable conditions that limit the simultaneous repassivation of all the corroded surfaces are driven by the anodic dissolution of β (Al₃Mg₂). Metastable processes that limit the hydration of metal ions while producing high local hydrogen concentration are more likely to involve the formation/decomposition of reactive hydride intermediates. E_{ptp} corresponds to the mixed electrode potential at which both metal dissolution and hydrogen evolution occur beyond some distance into the cavity, while i_{ptp} evaluates the catalytic activity of the corroding surfaces. The effective anodic charge transfer coefficient α_{eff} determined from the steepness of the potential drop estimates the contribution of Cl⁻ electromigration in response to local electrodisolution processes.

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1. Introduction

Single cycle anodic polarization has been widely used for investigating the repassivation behaviour of Al and alloys in chloride containing solutions [1–17]. A potential drop at high currents during the potential scan into the negative direction has been frequently detected [1–4,6–10,12–17]. This characteristic, illustrated for an Al-Mg-Si alloy in Fig. 1 [10], manifests a transition to more occluded local processes that limit the simultaneous repassivation of all the corroded surfaces [1,8]. The transition supported by the critical pit chemistry has been recognized [1–10]. The potential at the inflection (Fig. 1), designated as the pit transition potential E_{ptp} according to Yasuda et al. [2], corresponds to the thermodynamic driving force of Al dissolution on freshly created (filmed) surface rather than on initially passive surface as for the

pitting potential E_{pit} [3,10]. The associated current density i_{ptp} is proportional to the rate at which hydrolysis equilibrium is reached at a critical saturation concentration of Al³⁺ [10] and refs. therein], being represented by the general equation (1) to account for the contribution of OH⁻ (pH > 7):



Both E_{ptp} and i_{ptp} define the onset of metastable conditions that hinder the repassivation processes. The steepness or gradient of the potential decrease with current density at $E < E_{\text{ptp}}$ (Fig. 1) is proportional to the local acidity removal for full hydrolysis to be reached at the protection potential E_{prot} [10].

The response to repassivation in aftermath of microstructural effects (e.g. impurities, precipitate phase, solute-depleted region) [6,10,12] and of mechanical deformation (residual [13] and applied [9,16,17] stresses) is not fully clear. The not distinguishable inflection detected for commercially pure Al 1050 exhibiting either etched or crystallographic pits [10] suggests that the presence of a

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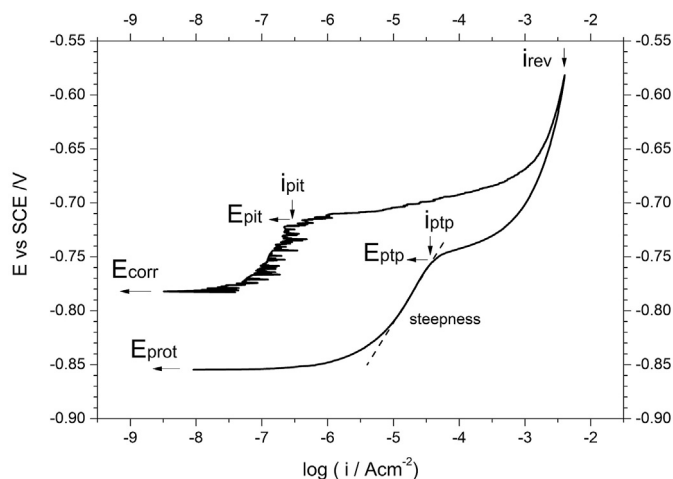


Fig. 1. Single cycle anodic polarization curve of Al 6082-T6 in 0.6 M NaCl (pH 6.5) [10], where i_{rev} represents the current density limit of the forward scan; E_{corr} – corrosion potential; E_{pit} and i_{pit} – pitting potential and the associated current density, E_{ptp} and i_{ptp} – pit transition potential and the associated current density; E_{prot} – protection potential.

salt layer in mass-transport limited repassivation is not mandatory. From studies with alloyed aluminium [6,10], E_{ptp} does not change if the critical feature is the electrochemical behaviour of a precipitate phase, as for Al 6082-T6 which intergranular corrosion is governed by the selective dissolution of Mg_2Si [10]. Conversely, E_{ptp} varies if the critical feature is a solute depleted region as in the case of Cu-containing alloys [6,10]. The shift of E_{ptp} to less negative values with the amount of corrosion [10] is consistent with the selective dissolution of Cu-rich particles producing less active Cu-depleted zones between the particles and the matrix [18]. Concerning the effect of mechanical stress on the response to repassivation, steeper potential gradients at the transition with accumulated strains by pressing have been reported for fine grained Al (99.9%) [9]. The opposite has been found for Al 2024-T3 subjected to residual elastic compressive stresses after removal of uniaxial tensile load [13]. A recent study with Al 2024-T3 and Al 7075-T6 under permanent load in bending has indicated that the effect of local stresses below the yield strength is enhanced with anodic processes localization during repassivation [17].

Al-Mg alloys are of special interest from the prospective of the understanding and achievement of the balance between mechanical performance and corrosion resistance. It is well known that the susceptibility to intergranular corrosion (IGC) and intergranular stress corrosion (IGSC) increases with $\beta(Al_3Mg_2)$ phase precipitation along grain boundaries. This phenomenon, known as sensitization, becomes significant with long-time exposure at elevated temperatures (50–200 °C). The nitric acid mass loss test (NAMLT) [19] is typically used for estimating the susceptibility to IGC in terms of the degree of sensitization (DoS) in mg/cm^2 of mass loss, being the traditional ranges of IGC susceptibility defined as: resistant ($DoS < 15 mg/cm^2$), intermediate ($15 mg/cm^2 < DoS < 25 mg/cm^2$) and susceptible ($DoS > 25 mg/cm^2$). Because of the faster dissolution than the matrix of the β phase in concentrated nitric acid, the mass loss increases due to grain fall-out with the amount and connectivity of β phase at grain boundaries. The interdependence between the exposure conditions (temperature, time and environment) and interrelated variables such as metallurgical, electrochemical and stress states, have been underlined in recent reviews reporting most of the relevant works on this argument and new experimental findings [20–23]. The critical temperature range 100–200 °C ($DoS > 25 mg/cm^2$) is determined by the appreciable

diffusion kinetics and volume fraction of β -phase [20]. However, long-time exposure at ambient temperatures promotes sensitization due to the high equilibrium β -phase volume fraction. Nucleation and growth of β phase at other lattice defects such as at the interface between the matrix and intragranular second-phase particles and at dislocations may occur [20,21]. The apparent β -phase continuity parameter, defined as the ratio between the average nearest neighbour distance (NDD) and the average diameter (\bar{d}) of β phase at grain boundaries, has been indicated as more adequate than DoS for predicting IGSC susceptibility [21]. A key aspect concerns the rate-controlling processes of IGC and IGSC propagation along the grain boundary between the β phase particles. The anodic dissolution of the β phase aiding the sustenance of the acidified pit-like chemistry for grain boundary diffusion of hydrogen and embrittlement has been considered in the IGSC mechanism of Al-Mg alloys [21–23].

In this paper, the effect of $\beta(Al_3Mg_2)$ precipitation at grain boundaries on the repassivation behaviour of a high content of Mg (>4 wt%) 5083-H111 Al alloy in 0.6 M NaCl (pH 6.5) is investigated by means of single cycle anodic polarization. The alloy specimens were isothermally treated at 150 °C in air during different times and characterized by XRD, SEM/EDS and metallographic analyses. The DoS and the mechanical properties were evaluated by conventional NAMLT and microhardness measurements.

2. Experimental part

The starting material was a commercial wrought sheet (thickness 1.5 mm) of 5083-H111 Al alloy with nominal composition (wt %) 4.3 Mg–0.6 Mn – 0.3 Fe – 0.2 Si – bal. Al (Aviometal Spa., Italy), present in the laboratory since 2006 (aged \approx 10 years aged at room temperature). Metallic specimens of dimensions 20×30 mm were wet ground up to 1200 grit using SiC papers, then polished with 4000 grit ($3 \mu m$) 3 M polishing paper, and cleaned with ethanol in an ultrasonic bath. Thermal treatment was carried out at 150 °C in an open to air oven during different times (from 24 to 360 h). The composition and microstructure of the untreated and isothermally treated specimens were evaluated by XRD, SEM/EDS and metallographic analyses. The diffractograms were collected using Philips PW 1830 diffractometer with $CuK\alpha$ radiation from 5 to 80° of 2θ . XRD data were analyzed with Diffrac plus EVA software (Master database, Bruker). SEM/EDS analysis of freshly-prepared specimens with surfaces polished up to 0.05 μm grain size of colloidal alumina (water-based dispersion) was performed at LEO 1430 scanning electron microscope (SEM) equipped with EDS spectrometer at the chamber pressure of 8×10^{-6} torr and 20 keV accelerating voltage. Another set of specimens was used for metallographic analysis, following a reported procedure [24]. Briefly, the surfaces were chemically etched by immersion in $(NH_4)_2S_2O_8$ (10 g/100 mL) at room temperature during 30 min and thereafter examined at Nikon Eclipse MA200 metallographic microscope coupled with JCV-C1380 digital photcamera. Nitric acid mass loss test (NAMLT) was used to evaluate the susceptibility to IGC in terms of the degree of sensitization (DoS) as guided by ASTM G 67 standard practice [19]. The specimens were immersed in HNO_3 (70%) during 24 h at room temperature after desmuting by 1-min immersion in 5% NaOH solution at 80 °C and 30-s immersion in HNO_3 (70%) with intermediate water rinse steps and final air drying. The DoS as mass loss (in mg/cm^2) was quantified from two replications. Micro-hardness measurements were performed following the micro-indentation standard practice ISO 14577/DIN 50359, using 1 N (0.1 kgff) onto the surface. Average Vickers hardness (VH) was calculated from five indentations for each test condition.

Electrochemical experiments were conducted at room temperature in stagnant naturally aerated 0.6 M NaCl (>99%, Aldrich) with

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