Pit transition potential in the repassivation process of Al Alloys

M. Trueba, I. Comotti, D. Cicolin, S.P. Trasatti
Department of Chemistry, Università degli Studi di Milano,
Via Golgi 19, 20133, Milan, Italy
monica.trueba@unimi.it

Introduction

This work reports on a systematic investigation of wrought Al alloys corrosion in NaCl solutions using single-cycle anodic polarizations or pitting scans (PS) (Fig. 1). The pit transition potential (E_{ptp}) associated with the first stages of surface repassivation was repeatedly identified as an inflection point in the reverse scan under certain experimental conditions [1,2]. Besides the current limit of the forward scan (I_{rev}), the effect on E_{ptp} of different experimental conditions such as pH, concentration of NaCl, and dissolved oxygen of the test solution was explored for Al-Mg-Si alloy 6082-T6.

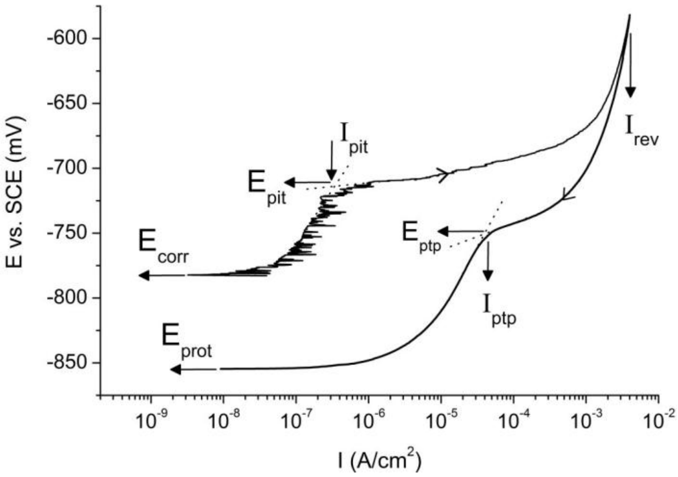

Figure 1: Schematic representation of electrochemical parameters: E_{corr} – open circuit potential; E_{pit} – pitting potential; I_{pit} – pitting current; E_{prot} – protection potential, E_{ptp} – pit transition potential, I_{ptp} – current at E_{ptp}; I_{rev} – forward current limit for scan reversal

Experimental part

Materials used were sheets of commercial wrought Al alloys 1050-H24, 6082-T6, 2024-T3, 7075-T6. Specimens (20x30 mm) were wet ground with abrasive silicon-carbide paper up to 1200 grit, then cleaned in an ultrasonic bath for 15 min with ethanol, dried in a stream of warm air and stored in a desiccator overnight. Before use, specimens were polished with 3μm cloth using ethanol and cleaned as above to remove remaining unevenness and/or possible defects originated from different rates of film growth with Al alloy composition. Single-cycle polarization was carried out at room temperature in NaCl (98 %, Aldrich) solutions prepared with MilliQ water. Different pH and concentrations were used. Some experiments were carried out in O_2-saturated solutions. Measurements were performed in a single-compartment O-ring cell with the working surface (1 cm^2) positioned upward, a Pt spiral and Luggin capillary reference probe with a saturated calomel electrode (SCE). After equilibration at the open circuit potential for 10 min., pitting scan was recorded at a scan rate of 10 mV/min up to a pre-selected current values (I_{rev}) for scan reversal. The experiment was ended at the lowest cathodic current value of the reverse scan. Experimental data were collected with a PC driven potentiostat (EG&G PAR 273A). At least five replicated experiments were carried out with freshly 3μm-polished samples. All the potentials in the text are referred to SCE. OriginPro 8 (OriginLab, Northampton, MA) was used for graphical plots and quantitative analysis. Average PS were calculated with replicated curves for each I_{rev}. Electrochemical parameters were determined as schematically depicted in Figure 1.

Results and discussion

With the aid of corrosion morphology characterization, it is obtained that the occurrence of the step at E_{ptp} is related to localized attack other than pitting. For all alloys, E_{ptp} variation was negligible with I_{rev}, conversely to the position of the inflection point in the current axe (I_{ptp}). The steepness of the potential depression at $E < E_{ptp}$, determined as the slope in the E-logI curve, as a function of log I_{ptp} is shown in Figure 2 for the alloys submitted to different I_{rev}. Al 6082-T6 with intergranular corrosion as the main form of localized attack shows a linear variation of the steepness with $\log I_{ptp}$, whereas for Al 2024 the steepness notably increases due to tunneling corrosion (Fig. 3a,b). The high strength Al 7075 with signs of environment-induced stress corrosion (Fig. 3c) shows a constant variation of the steepness as I_{rev} increases, in correlation with stress relaxation due to transgranular corrosion. Thus, the inflection point at the critical value E_{ptp} manifests difficulty for repassivation, which can be quantified by the steepness of the subsequent potential depression up to E_{prot} (Fig. 1). Tunneling corrosion in Al 2024 could be a consequence of limited repassivation as E falls below E_{ptp} [3].

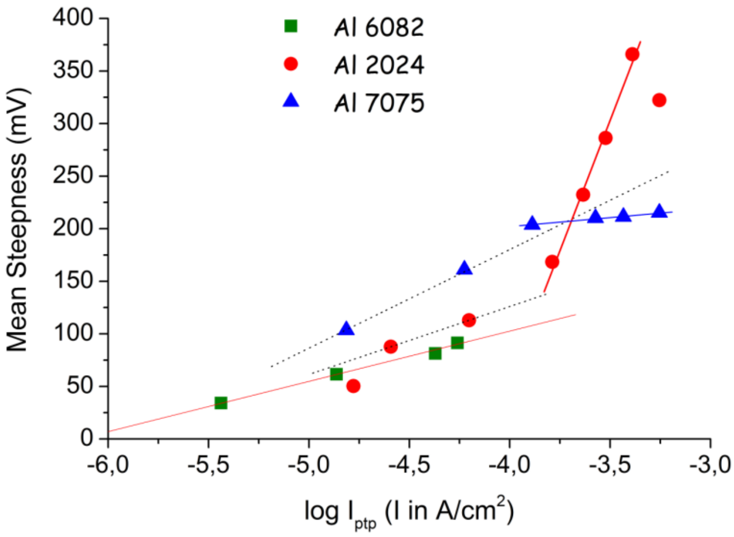

Figure 2: Relationships between the steepness of potential depression after the inflection point and log Iptp for the alloys subjected to different I_{rev} in near neutral 0.6M NaCl.

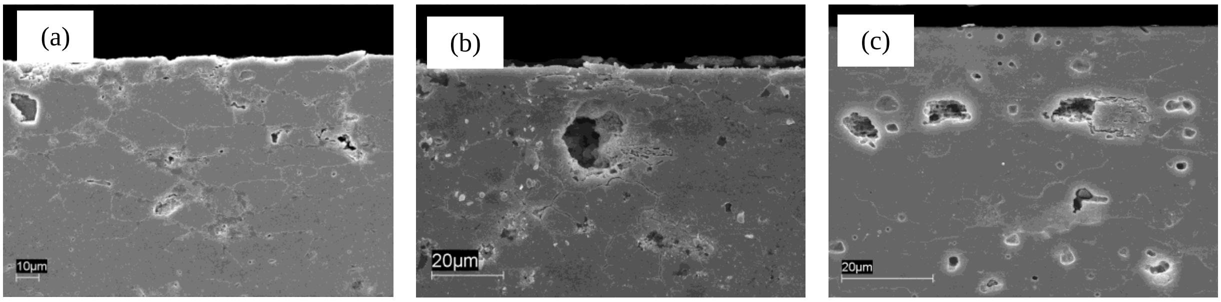

Figure 3: Section SEM images of Al alloys after pitting scan in near neutral NaCl with $I_{rev} > 1$ mA/cm^2: (a) Al 6082-T6; (b) Al 2024-T3; (c) Al 7075-T6

Figure 4 shows the results obtained for Al 6082 after experiments with different pH and concentrations of NaCl in the test solution. The notably steepness obtained with 0.1M NaCl correlates with the higher IG penetration observed on sectioned specimens by SEM. A tendency to pits opening as Cl^- concentration increases was indicated. The steepness, however, shows mainly a pH-independent behavior. The same trend was obtained with O_2-saturated solution. Also E_{ptp} does not depend on the solution pH and varies linearly with log c(NaCl) with a slope of about -90 mV. This value lies in the range reported for the variation of E_{pit} with log c (NaCl) [4]. Accordingly, the inflection point at E_{ptp} and the subsequent steepness for all pits surfaces to repassivate at E_{prot} are properties related with the critical chemistry of occluded corroded sites. This is supported by the fact that both magnitudes are more important in diluted NaCl with more occluded attack.

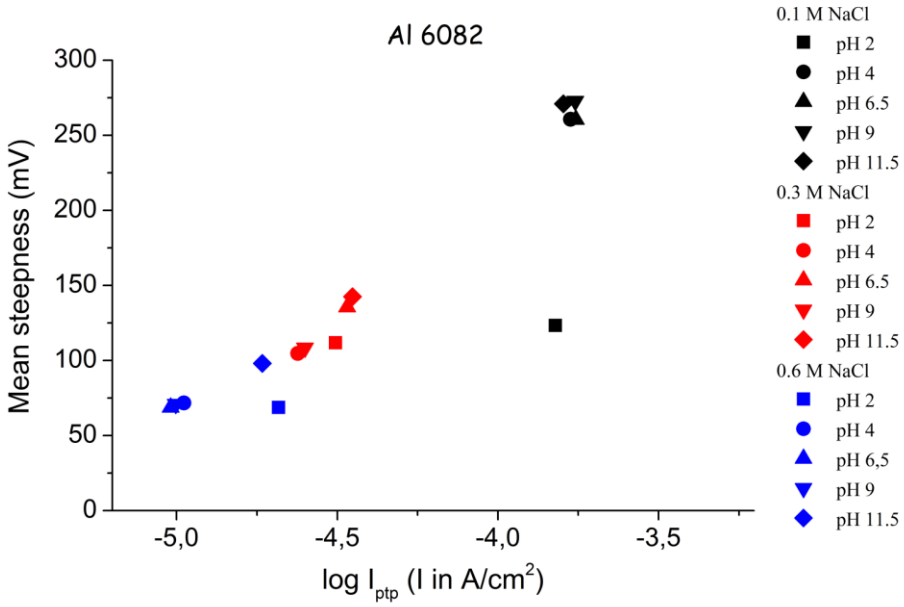

Figure 4: Relationships between the steepness of potential depression after the inflection point and log I_{ptp} for Al 6082-T6 submitted to I_{rev} of 2.5 mA/cm^2 in near neutral NaCl solution with different concentration and pH.

References:

[1] M. Trueba, S.P. Trasatti, Mater. Chem. Phys. 121 (2010) 523-533.
[2] M. Trueba, I. Comotti, S.P. Trasatti, Proceedings ASST 2012, Sorrento, Italy
[3] R.C. Newman, Corros. Sci. 37 (1995) 527.
[4] R. Newman, Electrochem. Soc. Interface (2010) 33.