CORROSION MECHANISM OF AL-ZN-IN ALLOYS IN CHLORIDE SOLUTIONS

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Abstract- The electrochemical behavior of Al-Zn-In alloys was investigated in chloride media by means of potentiodynamic techniques, complemented by Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Analysis (EDX) and Transmission Electron Microscopy (TEM). The influence of local alkalization produced by previous cathodization was analyzed at potentials more negative than the rest potential. The electrochemical response of alloys is given by the sum of those corresponding to the different present phases. Thus, the electrochemical behavior of each metal and bimetallic alloy (Al-In, In-Al and Zn-In) was analyzed in the same solution conditions at a potential region near the corrosion potential of the ternary alloy. The low solubility of In in Al favors its segregation at grain boundaries, where the formation of Zn-In alloys was detected. The initiation of the attack in the Al-Zn-In alloy is mainly localized in these zones. This is a consequence of the enhanced adsorption and surface accumulation of CI promoted by In at potentials more positive than - 1.1 V_{SCE}. Close similarities of the anodic behaviors of the Al-In and ternary alloys lead us to propose a mechanism where the In distribution plays the major role. The In dissolution from homogeneous solid solution phases allows an enrichment of this element at the Al and Zn rich phases by displacement reactions.

 $(Al,Zn)In + Cl \rightarrow InCl^{2+} + 3e^{-1}$

$$2 \operatorname{InCl}^{2+} + 3 \operatorname{Zn} \rightarrow 2 \operatorname{In}^{0} + 3 \operatorname{Zn}^{2+} + 2 \operatorname{Cl}^{-}$$

This, in turn, assures an accumulation of adsorbed Cl⁻, which maintains an active state of the Al matrix. Thus, the rapid Zn dissolution reaction ensures a better redistribution of In, so bringing the system towards potentials near those for Cl⁻ adsorption on In. The attack morphology was also analyzed in order to explain the smooth wide cavities embracing many grains.

Keywords- Aluminium, Al-Zn-In alloy, corrosion of Aluminium, Chloride adsorption.

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I. INTRODUCTION

Regarding commercially produced Al sacrificial anodes, there is little doubt today that Al-Zn-In base anodes present the best performance in seawater (Wolfson, 1994). The average operating potential of these anodes in this media is - 1.1 V vs. SCE. The activating elements (Zn, In) ensure its uniform dissolution and avoid polarization. Then, it seems reasonable that one way to obtain a fundamental understanding of this behavior lays in a better knowledge of the electrochemistry of the different phases constituting the ternary Al-Zn-In alloy. Previous studies have suggested that the initial step in the dissolution mechanism of the Al-In alloy can be interpreted in terms of a chloride adsorption process (Saidman et al., 1995). Thus, the more negative potential of zero charge (pzc) of In, compared with that of Al, allows the adsorption of Cl⁻ and the destabilization of the aluminium oxide film to occur at more negative values. The present contribution gives a better knowledge of the electrochemical response of the Al-Zn-In alloy. A commercial Al-Zn-In-Si anode and a ternary alloy, prepared in our laboratory, were used as working electrodes. The anodic behavior of pure metals (Zn e In) and the binary alloys Al-5%Zn, Zn-5%In, and Al-5%In are compared with that of the ternary Al-5%Zn-0.02%In in 0.5 M NaCl solution of pH 5. In order to obtain more information about mechanistic aspects of surface activation, the analysis of the synergistic effect produced by the deposition of Zn and In on Al, when their cations are present in solution, was also considered.

II. EXPERIMENTAL

The ternary alloy Al-5%Zn-0.02% In was obtained using pure Al, Zn and In (Aldrich Chemical Co., with impurities according to Table I). They were first etched in a 2% HNO₃ ethanol solution and then introduced in a quartz furnace with Ar atmosphere. It was heated at approximately 20 °C higher than the highest element melting point, shacked and then quenched in cold water. Due to the very low solubility of In and Zn in Al at room temperature (Baker and Okamoto, 1992) and the nominal composition used, the presence of rich In and Zn phases is expected. Higher solubilities, however, are possible as a consequence of quenching. A commercial Al-Zn-In-Si alloy, whose composition and impurities are also shown in Table I, was used for the sake of