ELECTROCHEMICAL TESTING OF Al-Zn-Mg SACRIFICIAL ANODES

M.A. Talavera, J. Juarez-Islas[1] and J. Genescá
Dpto. Ingeniería Metalúrgica. Facultad Química. Universidad Nacional Autonoma México, UNAM. Ciudad Universitaria. 04510 México.
1. Instituto Investigación Materiales, UNAM. Ciudad Universitaria. 04510 México D.F.

INTRODUCTION

Aluminum alloys suitable for cathodic protection have been developed in recent years, and the influence of alloying elements such as zinc (Zn), titanium (Ti), mercury (Hg), and indium (In) has been studied by several researchers [1-2].

It has been reported out [3] that in Al-IIB-IIA system, the α-Al solid solution and the τ-phase with a composition close to the $Al_2IIA_3IIB_3$ are present [4]. In the as-cast condition the main microstructure is formed by the α-Al solid solution and the second phase τ [4]. With reference to the Al-IIB-IIA ternary phase diagram [5], in the isotherm at 400°C (720 °F), there is present the α-Al solid solution plus eutectics of the IIA_2Al_3 and Al_2IIA_3IIB, which ensure via aging treatments a fine dispersion of those eutectics which help the non-passivation of the anode. In order to make the Al-Zn-Mg ternary system more efficient with respect to the superficial activation of the anode (preventing the formation of superficial aluminum oxide films) additions of IA are convenient [6] with the aim of precipitating the Al_3IA (δ') in grain boundary and matrix, by taking advantage of the fact that the Zn lowest the solid solubility of IA in the α-Al phase and also of the fact that Zn can be incorporated to the δ' phase.

EXPERIMENTAL RESULTS AND DISCUSSION

A representative microstructure observed in the as-cast ingot, consisted of α-Al dendrites with sizes between 130 to 150 μm (5.12 to 5.91 mils). In the interdendritic regions, the presence of an eutectic and black spherical particles was observed. The eutectic showed a white color with a maximum width of 10 μm (0.39 mils), always following the contour of the dendritic arms. This eutectic, instead of presenting a platelet morphology such as the one reported [3], showed the presence of rows formed by gray spherical particles.

The calculated electrochemical efficiency [7], ε, for the as-cast Al anode samples was 61.43%, corresponding to 1832 A-h/Kg . The closed-circuit potentials measured were in the range between -1.05 V (SCE) at 0 mA/cm^2 to -0.86 V (SCE) at 4.0 mA/cm^2 (25.81 mA/inch^2). The NACE [8] and DNV [7] tests specify that an Al anode should have a closed-circuit potential active to –1.0 V (SCE) and a ε between 2300 and 2700 A-h/Kg (1044.2 and 1225.8 A-h/lb.). Then the anode analyzed met the potential criterion, but appeared to exhibit only moderate efficiency. Theoretically, uniform anode dissolution will give maximum efficiency. Either secondary cathodic reaction on the same interface and/or mechanical grain loss due to local macro or microcorrosion cells will reduce the anode efficiency [9]. In Al-Zn alloys, Zn tends to be rejected to interdendritic zones or grain boundaries. This effect is favored by the cooling rate and the alloying element characteristics (lower melting point than aluminum). Under polarization, this local composition variation will favor the initiation and propagation of macro- and micro-local events (galvanic corrosion and pitting for example). These events are responsible for lowering anode efficiency by electrochemical or mechanical mass loss [9]. The low efficiencies shown by the studied anodes are similar to those obtained by Salinas et al [9] for Al-5%Zn alloy. A possible explanation is that the main efficiency loss can be ascribed to the secondary reactions, since they are produced by the relatively high content of impurities, particularly Fe and Cu, that cause local cell action. Electrochemical Impedance Spectroscopy, EIS, measurements were performed during the DNV test. It is evident from the electrochemical impedance data that the current density condition plays a critical role on the resistive property of the corrosion products, suggesting a significant change on the corrosion product property formed on the Al anode. Dark gray corrosion products were formed. The surface dissolution morphology exhibited a rough, pitted surface. The EIS diagrams showed evidence of both passivation and pitting. The lower electrochemical activity exhibited by the Al anode samples strongly suggests that secondary reactions may be the fundamental cause of this behavior. In our experiments, the EIS diagrams obtained at higher current densities show an inductive semicircle which could be attributed to pitting corrosion. The preferred dissolution morphology is general attack rather than pitting, since pitting attack has been correlated to less than optimal performance.

The shape of the impedance diagrams presents important differences. At high and medium frequencies two depressed capacitive loops are evident. At low frequencies an inductive loop was detected. These results are in agreement with those obtained by Barbucci et al [10] and other authors [11-13], although in their research unalloyed aluminum was studied. The capacitive behavior at high and medium frequencies might be due to the oxide passive film and the metal/oxide interface, whereas for the inductive behavior, an oxide/solution interface could be ascribed to the faradic processes.

ACKNOWLEDGMENTS

REFERENCES

1. A. R. Despic, *J. App. Electrochem.* 6 (1976):p. 499.
2. M. Salleh, Ph. D Thesis, UMIST, Manchester, U. K., 1978.
3. A.Barbucci, G. Cerisola, G Bruzzone and A. Saccone, *Electrochim. Acta*, 42 (1997):p. 2369.
4. R.J. Kilmer and G.E. Stonere, Light Weight Alloys for Aerospace Applications II, TMS, 1991, p.3.
5. D. A. Petrov, in Ternary Alloys, eds. G. Petzow and G. E. Effemberg, Vol. 7, 1993, p. 57
6. X. Zhand, Y. Wang, *Corrosion Science and Protection*, 7 (1) (1995):p. 53.
7. DNV Recommended Practice RP B401 (1993): "Cathodic Protection Design", Det Norske Veritas Industry AS, Hovik 1993.
8. NACE Standard Test Method "Impressed Current Laboratory Testing of Aluminum Alloy Anodes", NACE Standard TM0190-98. NACE International, Houston, 1998.
9. D.R. Salinas, S.G. Garcia and J.B. Bessone, *J. App. Electrochem.* 29 (1999):p. 1063.
10. A. Barbucci, G. Cerisola, P.L. Cabot and G. Bruzzone, *Materials Science Forum*, Vols. 289-292 (1998):p. 529.
11. J.B. Bessone, D.R. Salinas, C.E. Mayer, M. Ebert and W.J. Lorenz, *Electrochim. Acta* 37 (1992):p. 2283.
12. J.B. Bessone, C.E. Mayer, K. Juttner and W.J. Lorenz, *Electrochim. Acta* 28 (1983):p. 171.
13. J.H.W. DeWitt and H.J.W. Lenderink, *Electrochim. Acta* 41 (1996):p. 1111.