Reply to the comments of L. Tomcsanyi on the paper 'Influence of the heat treatment in the electrochemical corrosion of Al-Zn-Mg alloys'

P. L. CABOT

Departament de Química Física, Facultat de Química, Universitat de Barcelona, Avinguda Diagonal, 647, 08028 Barcelona, Spain

The authors of the above work do not feel that they misinterpreted pitting corrosion using polarization resistance, Tafel slopes and the equilibrium potential of the $Al_2O_3 \cdot 3H_2O/Al$ couple.

In the above paper, the polarization resistance data were only determined in oxygen free solutions and under steady state conditions from micropolarization experiments in order not to affect the open circuit potential (o.c.p.). In this case, the o.c.p. was about -1.2 V vs SCE and the alloys did not show pitting attack. In contrast, in aerated solutions, the corrosion potential (E_{corr}) was about -0.8 V vs SCE and pitting was demonstrated. No polarization resistance data were given in this latter case.

The Tafel data reported in the above paper were not obtained by the Tafel extrapolation method. They were obtained using a program which fits the experimental results to a difference of exponential terms over a small potential range near the o.c.p. This was only performed in a number of experiments simply to compare the behaviour of the alloys studied. No calculations on the corrosion rates were intended. The Tafel parameters were qualitatively interpreted according to the well known fact that greater Tafel slopes correspond to the more protective passive films.

The alloys studied in the above paper contained small amounts of intermetallic compounds which were not attacked in oxygen-free solutions. Polarization resistance and Tafel data permitted the effect of such intermetallic compounds on the properties of the passive film in the absence of pitting attack to be demonstrated. When pitting occurs, such determinations are, in fact, very difficult. The basic problem is the kinetic interpretation, which can only be achieved using a suitable model. The most favourable case appears when the anodic reaction remains steady and highly localized [1]. Several laboratories including our own are developing techniques to study pitting corrosion under steady state conditions.

The second question raised by L. Tomcsányi is that pitting (E_π) and corrosion potentials can not be related with calculated thermodynamic data. However, the authors of the above paper did not perform any calculations to relate such quantities. Instead, they simply compared such potential values as is usual when representing pitting and repassivation potentials on the Pourbaix diagram in order to establish the active and passive zones [2–4].

The third question refers to the use of an excess of sulphate when determining E_π. Pitting corrosion is a complicated phenomenon and several theories have been given [5]. In fact, L. Tomcsányi et al. [6] proved by a radiotracer technique that sulphate is adsorbed on the oxide film. They also proposed the chemical bonding of chloride at the oxide/solution interface as an initial step of heterogeneous reaction between chloride and the oxide film. However, this initial step is really a chemical adsorption. Therefore, the conclusion of L. Tomcsányi et al. [6], i.e. that all the theories of aluminium pitting corrosion involving the ab- or adsorption of chloride are misleading, is not correct.

The concentrations of chloride investigated by L. Tomcsányi et al. were in the range 10^{-2}–10^{-3} mol dm^{-3} while 1 mol dm^{-3} Na_2SO_4 was used as a supporting electrolyte. Sulphate cannot be simply a supporting electrolyte because it presents specific adsorption and, therefore, blocks the oxide surface sites where chloride may be bonded. Painot and Augustynski [7] have shown by ESCA that chloride and sulphate penetrate into the oxide film at o.c.p. and also that the chloride content increases with respect to the sulphate content when the critical potential is approached (i.e. the chloride content of the anodic film depends on the potential).

Therefore, two questions can be posed in relation to the mechanism proposed by L. Tomcsányi et al. If chloride simply reacts with the oxide film, why does pitting only appear from a certain critical potential? If E_π changes when sulphate is added to chloride solutions, what is the meaning of E_π when sulphate is absent. In a recent work of the authors [8] it is shown that additions of sulphate to chloride solutions shifts E_π in the positive direction, but the repassivation potential does not change significantly (the repassivation potential is much more reproducible and appears to better characterize pitting corrosion rather than E_π [9]). This cannot simply be explained by the migration transport of chloride. The role of migration transport in pit initiation is unclear because during the anodic sweep and in the conditions prior to pit initiation the anodic current is very small.

References

[1]   S. Barnartt, Electrochemical Nature of Corrosion, *in* 'Electrochemical Techniques for Corrosion Engineering' (edited by R. Baboian), NACE, Houston, Texas (1986) pp. 1–11.

[2]   J. Kruger, New Approaches to the Study of Localized Corrosion, in ibid., pp. 25–33.

[3]   M. Pourbaix, 'Lectures on Electrochemical Corrosion', Plenum, New York (1973) p. 271.

[4]   J. V. Muylder, Thermodynamics of Corrosion, in 'Comprehensive Treatise of Electrochemistry', Vol. 4 (edited by J. O'M. Bockris), Plenum Press, New York (1981), pp. 63–74.

[5]   H. Kaesche, Werks. und Korros. 39 (1988), 152.

[6]   L. Tomcsányi, K. Varga, I. Bartik, G. Horányi and E. Maleczki, Electrochim. Acta 34 (1989) 855.

[7]   J. Painot and J. Augustynski, ibid. 20 (1975) 747.

[8]   P. L. Cabot, F. A. Centellas, E. Pérez and R. Loukili, ibid. 38 (1993) 2741.

[9]   D. M. Aylor and P. J. Moran, J. Electrochem. Soc. 133 (1986) 868.