Oxide Film Growth Kinetics on Magnesium

Miguel Gonzalez-Torreira, Andrew Fones and Alison J. Davenport

The University of Birmingham
School of Engineering, Metallurgy and Materials
Edgbaston, Birmingham, B15 2TT

The passive layer formed on Mg has been studied in detail by Nordlien et al. [1-3] and found to be composed of a mixture of oxide/hydroxide, most of the it being amorphous hydroxide, but also with a thin, dense MgO layer. Bradford et al. studied the oxide film on Magnox in alkaline conditions [4] by ion beam analysis and suggested the possibility of a barrier layer of MgO at the metal surface of less than 0.1µm. Do and co-workers [5] found that the "bulk" oxide film growth on Mg follows an inverse logarithmic kinetics by using Auger spectroscopy and XPS analysis in well defined atmospheres. The aim of the present work is to determine the growth kinetics of this film.

The usual method to measure the rate of growth of passive films is by monitoring the decay in current with time at a fixed potential. However these measurements are difficult to make as the current decay takes place over several orders of magnitude in current and time. Also it is necessary to know the initial state of the film and the iR drop to compare between different models of film growth.

In this work the oxide film growth kinetics of commercial purity magnesium (99.99%) and Magnox (0.8% Al) in alkaline solutions have been studied. The films were grown galvanostatically, which avoids iR drop problems, and means that it is not necessary to know the starting conditions, therefore allowing comparison of different film growth models.

Samples were polished and then cleaned with ethanol and etched in citric acid to remove any bulk oxide layer formed on the surface and to give a consistent initial starting condition. Fig.1 shows the V-t diagrams for several fixed currents in a NaOH solution at pH 13. The voltage grew linearly up to a certain value were the curve leveled off. The linear part was used in the analysis. By assuming negligible dissolution, a plot (1/i)dV/dt against lni allows us to discriminate between different oxide film growth models and estimate the growth parameters [6]. Fig.2 shows the plot for Magnox.

Film growth kinetics of both pure magnesium and Magnox were found to be similar. The data were found to fit the Cabrera-Mott model [7], assuming negligible film dissolution. The activation distance was of the order or 0.1nm for both pure Mg and Magnox, values physically reasonable given the assumptions involved in the experiments.

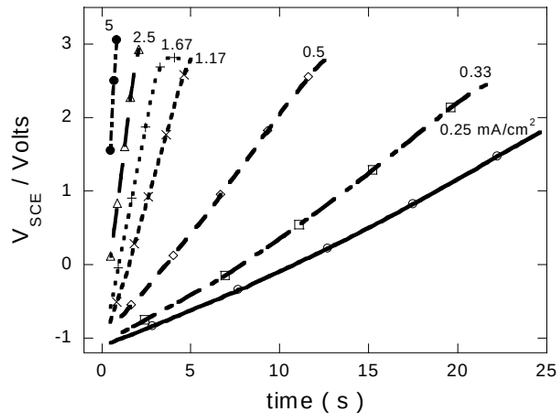

Figure 1. V-t plots for Magnox at different fixed current densities in a NaOH solution, pH 13

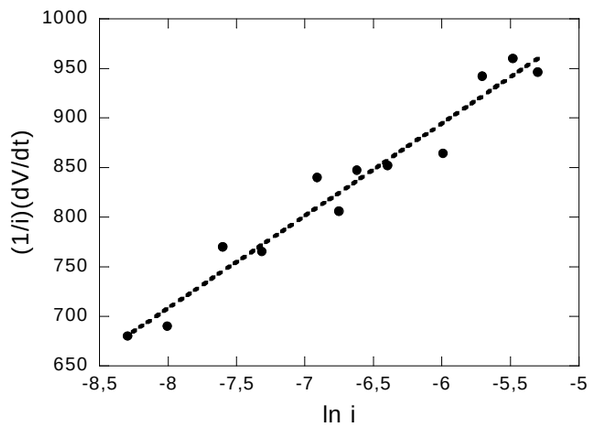

Figure 2) Plot of (1/i)dV/dt vs lni for Magnox in NaOH pH 13

[1] J. Nordlien, S. Ono, N. Masuko and K. Nisancioglu, J. Electrochem. Soc., **142**, 3320 (1995)
[2] J. Nordlien, K. Nisancioglu, S. Ono and N. Masuko J. Electrochem. Soc., **143**, 2564 (1996)
[3] J. Nordlien, K. Nisancioglu, S. Ono and N. Masuko J. Electrochem. Soc., **144**, 461 (1997)
[4] P.M. Bradford, B. Case, G. Dearnaley, J.F. Turner and I.S. Woolsey, Corr. Sci., **16**, 747 (1976)
[5] T. Do, S.J. Splinter, C. Chen and N. S. McIntyre, Surf. Sci., 387, **192** (1997)
[6] A. J. Davenport and B. K. Lee, in "Corrosion Science: A Retrospective and Current Status -- In Honor of Robert P. Frankenthal", Ed. G. Frankel, The Electrochemical Society Proceedings Series, Pennington NJ, (2002).
[7] N. Cabrera and N. F. Mott, Repts. Prog. Phys., **12**, 163 (1948/9)