A Feasible Strategy for the Collection of Kinetic Data for Complex Electrochemical Systems such as Hard Chromium Plating.

A. Hubin[1], S. Baré[1], C. Dan[2], B. Van Den Bossche[2], J. Deconinck[2]

[1]Dept. Metallurgy, Electrochemistry & Materials Science
[2]Dept. Electrical Engineering
Vrije Universiteit Brussel
Pleinlaan 2, B-1050 Brussels, Belgium

Hard chromium plating from chromic acid solutions is still, despite the toxic properties of hexavalent chromium, widely used in diverse applications. Very often, complex shaped parts (for example in the automotive applications) are plated to give them the required wear resistance and corrosion properties. For these parts the demands on thickness distribution are very high, requiring an optimised reactor design.

In the group of Deconinck et al. numerical tools are developed [1] to calculate the current density distribution in electrochemical reactors. The accuracy of the calculation depends, amongst others, on the correctness of the kinetic input data of the electrode reactions. This is a major difficulty in the case of hard chromium plating. Altough the electrodeposition of chromium has been practised for decades, and in spite of a considerable research effort [2], the mechanism is still open to discussion.

Our group has a large experience in the elucidation of the reaction mechanism of electrodeposition reactions [3-7]. The usual combination of electrochemical (such as linear sweep voltammetry, chronoamperometry, impedance measurements) and spectroscopic techniques (such as SEM, AES, XPS, Raman spectroscopy) to come to a complete understanding of a reaction mechanism, and a quantitative determination of the relevant kinetic parameters, is hardly applicable in this case.

Due to the complex chemistry of the chromium system, the necessity to use both a catalyst and (organic) additives and the wide range of plating conditions (temperature, bath composition, current density) to be considered, the number of parameters to be taken into account for a general mechanistic investigation is too high.

Therefore, for the purpose of performing calculations to find an optimal reactor design for a specific application, a different approach is proposed. It consists of an experimental and a modelling part. In the experimental part, relevant conditions on solution composition and temperature are considered. The polarisation behavior is monitored on a rotating disk electrode. The current efficiency is determined by anodic stripping. The polarisation data are then analysed in the modelling part using a dedicated software [8], based on the dilute solution model and taking into account multiple heterogeneous and homogeneous reactions. The result is a 'functional' mechanism for the chromium deposition describing the polarisation behavior within the range of considered conditions.

Figure 1 shows one example of regression of a physical model, taking different electrochemical and chemical steps into account, to experimental data. The model and the relevant parameters will be discussed.

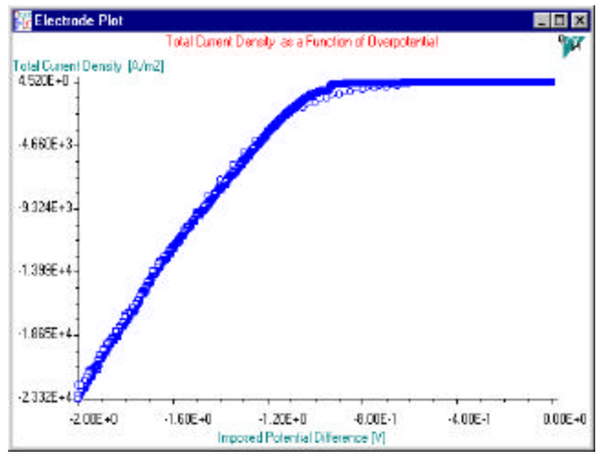

Fig.1: Polarisation behavior of 1M CrO_3 with 0.0127M H_2SO_4 on a Cr preplated Pt rotating disk electrode (1000 rpm) at 60° C. The open circles are the calculated points.

References

[1] B. Van Den Bossche, L. Bortels, J. Deconinck, S. Vandeputte, A. Hubin, J. Electroanal. Chem., **411** (1996) 129
[2] N.V. Mandich, Plating and Surface Finishing, May (1997) 108 & June (1997) 97
[3] S. Vandeputte, E. Verboom, A. Hubin and J. Vereecken, J. Electroanal. Chem., **397** (1995) 249
[2] D. Gonnissen, S. Vandeputte, A. Hubin and J. Vereecken, Electrochim. Acta, **41** (1996) 1051
[3] S. Vandeputte, A. Hubin and J. Vereecken, Electrochim. Acta, **42** (1997) 3429
[4] W. Simons, D. Gonnissen and A. Hubin, J. Electroanal. Chem., **433** (1997) 141
[5] D. Gonnissen, W. Simons and A. Hubin, J. Electroanal. Chem., **435** (1997) 149
[6] D. Gonnissen, W. Langenaeker, A. Hubin and P. Geerlings, J. Raman Spectrosc., **29** (1998) 1031
[7] W. Simons, D. Gonnissen and A. Hubin, ECS Proceedings, Proc. Vol. **97-27**, Ed. M. Datta, p. 124
[8] PIRoDE software manual, Elsyca NV, Brussels, www.elsyca.com.

Acknowledgement

This research project was sponsored by the EC under contract number BRPR CT98-0800 and by the Vrije Universiteit Brussel under project GOA11.