Samarium Salts as Corrosion Inhibitor Species for Metals in Aqueous Solution

Luis H. Del Ángel, D. Beltrán, Luis A. Godínez, Raúl Ortega and Yunny Meas[*]

Centro de Investigación y Desarrollo Tecnológico en Electroquímica S.C.
Parque Tecnológico Querétaro. San Fandila, Apdo. Postal 064, 76700
Pedro Escobedo, Querétaro, México
Tel. 52-(4)-211-60-70, Fax 52-(4)-211-6001,
yunnymeas@cideteq.mx

H. Sánchez

Universidad Autónoma Metropolitana-División Iztapalapa
Departamento de Química

Abstract

In recent years the study of rare earth compounds for the inhibition of the aqueous corrosion of metals, has been an intensive area of research around the world[1-3]. Hinton, Mansfeld and co-workers for instance,[4-6] have reported that Cerium and other rare earth salts effectively decrease the corrosion rate of aluminum on neutral aqueous solutions. Based on several experimental observations, they have postulated that the oxygen or solvent reduction event (coupled to the oxidation of the metal substrate), increases the local pH at the metal solution interface which in turns results in the formation of a hydrated oxide insulating film that protects the substrate from further corrosion attack. In a similar fashion to the phenomena studied by these researchers, we have also observed that Samarium salts excerpt a inhibition effect on the corrosion rates of steel in aqueous NaCl solutions[7]. We for instance measured a 20 time decrease in the corrosion rate of 409L steel samples when these were previously treated with aqueous Sm solutions. We believe that the protection mechanism by which this compound decreases the corrosion rate of steel and other metallic substrates, could be similar to the one postulated for other rare earth compounds and therefore we decided to study in detail this subject.

Cyclic voltammetry measurements of Sm in concentrated NaCl solutions show that, as expected, the Samarium species are essentially inert in the potential range that defines the solvent stability window. EQCM studies however, show that a protecting film is formed in the presence of Sm salts when other species in the electrolyte are electrochemically formed. In this way, the reduction of dissolved oxygen, or the reduction of the solvent at more negative potentials, result in the formation of protective Sm-based films of specific morphologies that clearly depend on the current density and on the nature of the reduction products. Using platinum substrates modified with Sm films prepared at different potentials, we carried out ESM studies that allowed us to correlate the film-formation potentials with the different thickness and porosity of these films. The obtained results show that whereas low-thickness dense films are formed as a consequence of the reduction of oxygen, massive and highly porous films are synthesized when the solvent is electrochemically reduced (obviously a compromise between thickness and low porosity is required to obtain good quality protecting films). The high porosity of the films is therefore directly related to the formation of gaseous hydrogen and the amount of hydrated oxide deposited is proportional to the product of the current density and the deposition time. Additional experiments with de-oxygenated solutions at different deposition potentials, further suggest that the film formation mechanism only obeys to the amount of electrochemically generated hydroxyl groups. Mass-deposition curves for solutions electrolyzed at different potentials in the presence and in the absence of oxygen, revealed that the mass deposited during film formation is additive and independent on the formation of gaseous hydrogen, which seems to only affect the porosity of the film. These observations have led us to suggest that, as in the case of the Cerium films studied by Hinton, Mansfeld and co-workers, the electrochemically induced increase in the local pH at the metal-solution interface, happens to be the responsible factor for the precipitation of a non-soluble Sm based film that also seems to be stable on neutral or basic solutions but pretty easy to remove with lightly acidic solutions.

Although deposition experiments on different metals indicate that the formation of these films seem to be relatively independent on the supporting substrate, its formation on iron, aluminum or other potentially important metals, depend on an oxidation event that necessarily is coupled with a reduction process that results in the formation of a protective film in the presence of aqueous samarium. Studies on the optimization of the deposit formation from aqueous solutions of Sm for steel, aluminum and other metals, are under way in our laboratory.

REFERENCES

[1] Böhm, S.; Greef, R.; McMurray, H. N.; Powell, S. M.; Worsley, D. A., *J. Electrochem. Soc.*, **2000**, *147*, 3286-3293.

[2] Hinton, B. R. W.; Arnott, D. R., "The Characteristics of Corrosion Inhibiting Films Formed in the Presence of Rare Earth Cations" in *Microstructural Science*, Vol. 17, Editors: Kenny, P. J.; Cole, G. S.; Northwood, D. O., Wylie, J.; Vander Voort, G. F., 311-320, 1988.

[3] Hinton, B. R. W., "Corrosion Prevention and Control" in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 21, Editors: Gschneidner, K. A.; Eyring, L., 29-92, 1995.

[4] Mansfeld, F.; Lin, S.; Kim, S.; Shih, H., *Electrochem. Acta*, **1989**, *34*, 1123-1132.

[5] Hinton, B. R. W.; Arnott, D. R.; Ryan, N. E. *Mater. Forum*, **1986**, *9*, 162.

[6] Mansfeld, F.; Wang, Y.; Shih, H., *Electrochem. Acta*, **1992**, *37*, 2277-2282.

[7] Ortega, R.; Beltrán, D.; Meas, Y.; Becerril, A., *J. Braz. Chem. Soc.*, **1997**, *8*, 149-152.