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Influence of the Chloride to Chromate Ratio on Zinc Corrosion Inhibition
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Beamline(s): X10C

Introduction: Chromate is known to be a very effective corrosion inhibitor for a wide range of metals and alloys. However, it is also well known that chromium is toxic in the hexavalent state and alternatives for its replacement are widely requested. Both chromate and chloride ions are strongly adsorbed on a metal surface [1] and significantly affect corrosion resistance of the metal. The aim of this study was to find the effect of the chromate to chloride ratio on the corrosion of zinc surfaces. The understanding on the influence of the ratio on the mechanism of chromate inhibition can be beneficial for a formulation of new chromate free inhibiting systems.

Methods and Materials: Polished zinc specimens were treated in saturated strontium chromate solution (8.9 mmol l^{-1}) with addition of sodium chloride in the range from 0 to 1000 mmol l^{-1}. In the next step the relative amount of chromate on the zinc surface was analyzed by Fourier Transformed Infra-Red Spectroscopy (FTIR), free chromate and chloride surface concentration by Ion Chromatography (IC) and the concentration of Cr(VI) at the surface by X-ray absorption near-edge structure [2] (XANES). Beside the mentioned techniques Scanning Kelvin Probe (SKP) measurements of the Volta potential distribution and the argon to air transition [3], as well as Secondary Ion Mass Spectroscopy (SIMS) analysis were used. The same measurements were performed after an exposure of specimens in wet air at relative humidity 95 % for 16 and 500 hours.

Results: An increase in the chloride concentration in the treating solution from 0 to 1000 mmol l^{-1} had only little effect on the concentration of chromate at the zinc surface. The total chromium surface concentration decreased by about 20 % and the Cr(VI) to total chromium ratio was at about 30 % in the whole range of chloride concentrations. Free surface chloride concentration increased sharply from 1 to more than 80 mg m^{-2}. The increase in the chloride to chromate surface ratio caused change in the Volta potential to negative values and increased the oxygen adsorption ability to the zinc surface and consequently increased the rate of the formation of corrosion product. On the basis of the results, a critical ratio of chloride to chromate molar concentrations both in solution and on the zinc surface was found.

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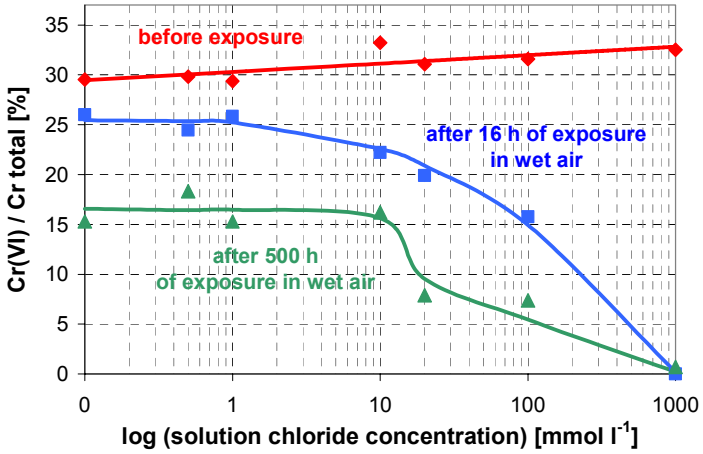
References:
[1] J.D. Ramsey, L. Xia, M.W.Kendig, R.L. McCreery, “Raman Spectroscopic Analysis of the Speciation of Dilute Chromate Solutions,” Corrosion Science, **43**, *1557-1572*.
[2] M.W. Kendig, A.J. Dawenport, H.S. Isaacs, “The Mechanism of Corrosion Inhibition by Chromate Conversion Coatings from X-Ray Absorption Near Edge Spectroscopy (XANES),” Corrosion Science **34**, *41-49*.
[3] A. Nazarov, D. Thierry, “Determination of the Efficiency of Surface Treatments on Metals by Scanning Kelvin Probe,” Eurocorr ‘99, Aachen, Germany, 1999.



The Cr(VI) to total Cr ratio on the zinc surface treated in saturated strontium chromate solution (30 minutes, laboratory temperature) with different chloride concentration.