Molecular Structure of Chromate Conversion Coatings

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Corrosion inhibitors such as Chromate Conversion Coating (CCCs) have been around for many years, and though their properties are well known, the relationship between corrosion inhibition and molecular structure has been only studied sporadically. The commercial Al-Cu alloy AA2024-T3 is used extensively in the aircraft industry and is particularly important for the US Air Force. The alloy is susceptible to localized corrosion due to the presence of heterogeneous microstructures on the alloy surface. To improve its corrosion resistance, the alloy is normally given a chemical surface treatment by immersion in chromate solution, which forms a protective CCC. Chromate ions are one of the most effective aqueous corrosion inhibitors for a range of commercial metals and alloys. Unfortunately, chromates (Cr^{6+}) are known to be toxic and suspected carcinogenic properties; therefore, the development of chromium-free treatment has become a priority. The knowledge of the effects of the chemical structure of the CCC on its protective action would enable the synthesis of inhibitors with tailored properties.

CCCs are generally amorphous, hence characterizing its structure is a problem is well suited for EXAFS due to the ability of probing disordered systems lacking in long range order.[1-3] The molecular structure of the CCC is believed to be composed of a precipitated hydrated Cr^{3+} compound, which adsorbs the Cr^{6+}.[4-9] Only one of the sited studies used EXAFS to investigate the CCC structure. The main focus of this work is to investigate in greater detail the structure of the CCC using EXAFS and associated molecular modeling.

Fluorescence EXAFS was performed on beamline X10C at NSLS. A typical file created by the ATOMS program (using Structural parameters reported by Wilhemi[14]) was put into the FEFF6 program and the theoretical phases and amplitudes were generated using the *ab initio*, single- and multiple-scattering code FEFF6.[12,13] Data reduction of experimental EXAFS fitting and simulation were accomplished using the WinXAS v2.3 analysis software.[10-11] For energy reference the K edge of a Cr foil was measure before every sample. Pre-edge background subtraction and normalization was performed by fitting a linear polynomial to the pre-edge region and a cubic polynomial to the region after the edge of the absorption spectrum. A smooth atomic background, $\mu_0(k)$, was obtained using cubic splines. EXAFS fitting and simulation were performed using the standard EXAFS formula.[1] The fitting range in k space, the number of spline knots, and k-weighting were optimized to obtain a rigid background curve at low k. Minimization of low R peaks in the Radial Structural Function (RSF) was obtained by Fourier transformation of the experimental $\chi(k)$ function with k^3 weighting, which was multiplied by a Bessel window into the R space.

Following the fitting routine using the WinXAS package, the models for the theoretical and experimental Cr mixed oxide compound were found to be in good agreement. Results suggest that the CCC is similar to a Cr mixed oxide compound. The CCC was found to contain octahedrally coordinated Cr^{3+}-O and The Cr^{6+}-O were in a tetrahedral arrangement. Slight differences might be due to higher disorder in the CCC and the presence of other elements. Also, curve fitting indicated a lower C^{6+}/Cr^{3+} ration in the CCC as compared to the model mixed oxide, indicating that additional reduced Cr species exists in the conversion coating.

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