

Novel Synchrotron-based Spectroscopic Investigations on the Chromate Conversion Coatings Formed on AA2024-T3 - D. Chidambaram, C.R. Clayton, and G.P. Halada (State University of New York at Stony Brook)

Dichromate based solutions have been used as corrosion inhibitors for nearly a century (1, 2). Toxicity and mutagenic effects of hexavalent chromium are well-known (3, 4). The development of alternative coatings requires the precise knowledge of the underlying mechanisms of protection offered by hexavalent chromium, which are unclear and still under investigation.

Although a variety of surface analytical tools have been utilized to study the interaction of chromates with aluminum, the use of synchrotron based Fourier transform infrared (FT-IR) spectroscopy and X-ray absorption near edge spectroscopy (XANES) are particularly attractive since these experiments can be performed at ambient conditions with no damage to the coating as might be expected from techniques imposing stringent conditions such as ultra high vacuum, extreme temperature etc.

The ability of FT-IR spectroscopy to be operated in various modes makes it a very attractive analytical technique. However, thin films and coatings are studied using reflection-absorption and transmission modes only. For the first time synchrotron radiation based FT-IR spectroscopy with a grazing angle objective (GAO) has been used to study a chromate conversion coating (CCC) formed on aluminum alloy. A spectrum was obtained in the reflection-absorption mode for comparison. The use of GAO leads to increased sensitivity to surface species. Synchrotron radiation based grazing angle infrared spectroscopy (SR-GAIRS) was observed to increase the sensitivity to chromate by nearly an order of magnitude when compared to near reflection-absorption infrared spectroscopy (RAIRS) mode of the FT-IR.

Defects or mechanical damages in CCC's are protected without further treatment by "self-healing" properties (5-7). "Self-healing" has been associated with migration of chromates to actively corroding sites (8-13). The formation of a protective Al(III)-Cr(VI) complex at damaged sites was first suggested by Abd Rabbo *et al.* (14). McCreery *et al.* later proposed and demonstrated the formation of an Al(III)-Cr(VI) complex in pits (9, 15). Earlier work from this laboratory has verified the presence of Al(III)-Cr(VI) complex in scratches (12, 13). In this work, we have performed a set of novel investigations involving scratching of the AA2024-T3 substrate in a controlled and systematic manner prior to the formation of CCC and studied the variation in hexavalent chromium content in the coating using XANES. We have attempted to explain the relationship between Cr(VI)/Cr(Total) ratio to the number of scratches in mathematical terms with physical significance.

Acknowledgements

The U.S. Air Force Office of Scientific Research under contract F4962093-1-0218

supported this work. Lt. Col. Paul Trulove, Ph.D. served as contract officer. Research was carried out in part at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy. We thank Lisa M. Miller, Nebojsa Marinkovic (U10B beamline) and Larry Ferreria (X10C beamline) for their help. The support received from staff and personnel of the NSLS are gratefully acknowledged.

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