

# X-Ray Absorption Study of Chromate Conversion Coating Degradation with Dehydration under Aging or Moderate Heating

V. Laget, R. Buchheit (Ohio State U.), C. Jeffcoate and H. Isaacs (Brookhaven National Laboratory)

Abstract No. Iage7852

Beamline(s): X10C

**Introduction:** Chromate conversion coatings (CCCs) are commonly used on all types of aluminum alloys in manufactured products ranging from aircraft to automotive components. These thin coatings appear to provide both passive barrier protection by preventing an aggressive environment from contacting the alloy substrate, and active corrosion protection, in which the coating is able to self-repair. This property is thought to be related to a reservoir of labile  $\text{Cr}^{6+}$  that can be released into the attacking solution and migrate to locally corroding areas to inhibit further damage (1).

The self-healing properties of chromate conversion coatings are temporary in nature and will degrade noticeably in a matter of weeks after coating formation or when exposed to moderate temperatures. Previous XANES results show that loss in self-healing is not related to reduction of Cr(VI) in the coating, but rather to its immobilization associated with dehydration (2). Understanding the mechanism of Cr(VI) release and its immobilization with aging or heating is complicated by the fact that the exact chemical nature and local structure of the amorphous Cr(III)-based coating (hydroxide, hydrated oxide, or oxo-hydroxide), the nature of the Cr(VI) species in the reservoir (dichromate, chromate or bichromate), and the type of bonding between those two have not yet been fully elucidated.

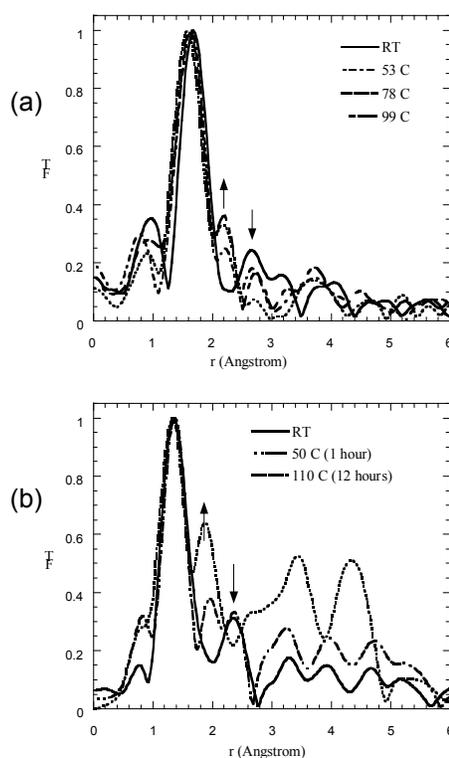
**Methods and Materials:** CCCs on Al alloy 2024-T3 were submitted to soft thermal treatments (53, 78 and 99°C during 15 minutes) and measured by EXAFS at the Chromium K edge to observe structural changes occurring during dehydration. Amorphous  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  was diluted in BN powder (5 mg in 200 mg) and pressed into pellets. The fluorescent intensity was recorded with a 13-element Ge Canberra detector on samples tilted at 45° to the incident beam. Three scans were recorded for each sample and data treatments were performed with the software LASE (3) as described elsewhere (4). The measurements were not phase corrected.

**Results:** The variation of the magnitude of the Fourier transform is shown **Figure 1**. The peak associated to the shortest Cr-Cr distance seems to decrease with the temperature while a third peak corresponding to a shorter Cr-Cr distance is increasing. The same variation of the peaks with temperature is observed on amorphous  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ , showing that the structural rearrangement involves the first Cr(III)-Cr(III) neighbors and not the Cr(III)-O-Cr(VI) bond (no Cr(VI) present in  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ ). Upon dehydration, a second phase is formed with a closer Cr(III)-Cr(III) distance. A simple tilting of octahedra from a corner-shared structure to an edge-shared structure may be at play, leading to a more compact structure and possibly to an entrapment of the Cr(VI) species.

**Acknowledgments:** This work is supported by the Army Research Office and the Strategic Environmental Research and Development Program under contract no. DACA-72-99-C-0002. H.S.I was supported by the Department of Energy, Division of Materials Sciences, Office of Science under contract no. DE-AC02-98CH10886. C.S.J. was supported by the Air Force Office of Scientific Research under contract no. F49620-96-1-0479.

## References:

- (1) J. Zhao, G. Frankel and R. McCreery, "Corrosion Protection of Untreated AA2024-T3 in Chloride Solution by a Chromate Conversion Coating Monitored with Raman Spectroscopy," *J. Electrochem. Soc.*, **145**, p. 2258-2264, 1998.
- (2) V. Laget, H. Isaacs, C. Jeffcoate, R. Buchheit, "Thermal Stability and Aging Characteristics of Chromate Conversion Coatings on Aluminum Alloy 2024-T3," *Proc. Electrochem. Soc.*, **99-26**, p. 173-182, 2000.
- (3) LASE, LURE, Université Paris-Sud, Orsay, Fr.
- (4) V. Laget, H. Isaacs, C. Jeffcoate, R. Buchheit, "Thermally Induced Degradation of Chromate Conversion Coatings on Aluminum Alloy 2024-T3," *ATB Metallurgie* (in press).



**Figure 1.** Magnitude of the Fourier transforms obtained for CCC (a) and amorphous  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  (b) with increasing dehydration (heating time of 15 min or as indicated).