

# ***In-situ* XANES Study of Formation of Chromate Conversion Coatings on Aluminum and Its Alloys**

K. Sasaki<sup>a</sup>, H.S. Isaacs<sup>b</sup>, C.S. Jaffcoate<sup>a</sup>, H. Lee<sup>b</sup>, V. Srinivasamurthi<sup>c</sup>

<sup>a</sup> The Fontana Corrosion Center, The Ohio State University, Columbus, Ohio 43210, USA

<sup>b</sup> Brookhaven National Laboratory, Upton, New York 11973, USA

<sup>c</sup> Northeastern University, Boston, Massachusetts 02115, USA

X-ray adsorption near-edge structure (XANES) offers a powerful technique for the *in-situ* study of inhibiting species in passive films and in solutions since it determines metal concentration during dissolution processes [1]. This technique also allows the inhibiting effects of chromate in solutions and the chromate conversion coatings (CCC) films to be examined [2, 3]; the CCCs have been used extensively for aluminum and its alloys in the aerospace industry. The CCC involves a number of Cr(III) and Cr(VI) species, and Cr(VI) is believed to be responsible for the ability of the CCC to protect scratches generated on a metal surface from further electrochemical degradation. Thus, the more numerous Cr(VI) ions in the CCC may impart the better protection. A distinct pre-edge peak at *ca* 5993 eV in the XANES spectrum is observed when hexavalent chromium Cr(VI), such as in  $\text{CrO}_4^{2-}$  is present. The ratio of height above the edge (arising from all chromium species present) to the pre-edge height (only Cr(VI)) provides a quantitative measure of Cr(VI) concentration.

We have developed a novel electrochemical cell, in which one side of a specimen is covered with a plastic film transparent to X-rays, as schematically shown in Figure 1. The cell is completely sealed except for a tube connected to a solution reservoir. By lifting the chromate solution reservoir, hydrostatic pressure in the cell is increased so the solution can flow into the cell and inflates the membrane with the solution (Figure 1(a)). By lowering the reservoir produces a fall in pressure in the cell, and the solution is drained off the cell and the membrane is sucked, thereby the surface reaction is suppressed (Figure 1(b)). The specimen surface is thus subjected to repeated exposures to the treatment solution. By repeating this process and a XANES measurement between immersions, changes on the treated surface can be characterized. A commercial chromate solution, Alodine 1200 ( $7.5 \text{ g l}^{-1}$ ), was used. Moreover, if the treatment solution is not completely drained from the cell and a thin film of the solution remains on the specimen surface, it is possible to monitor the change in Cr(VI) ions in the remaining solution layer with exposure time. It is to be noted that the *in-situ* XANES measurement with this new cell is quite unique since all known investigations of CCC have been conducted *ex-situ*. Data acquired for aluminum and its alloys subjected to repeated/continuous exposure to the chromate solution with this new cell are presented.

Copper additions to aluminum, usually in combination with other elements, improve mechanical properties through appropriate heat treatment. The previous results showed that the concentration of Cr(VI) in the CCC formed on an Al-Cu alloy is greater compared

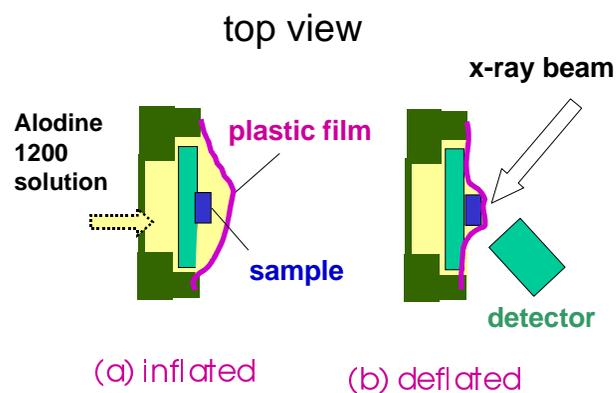
with that formed on pure aluminum [3]. Thus one may expect that the concentration of Cr(VI) increases with an increase in Cu content in aluminum alloys. *In-situ* XANES measurements were performed on a series of binary Al-Cu alloys (0-5% Cu) to examine variation that appears to be dependent on Cu content. On the basis of the experimental results, the kinetics of the CCC formation and the effect of Cu alloying element content on the ratio of Cr(VI)/Cr(III) will be discussed.

## **Acknowledgment**

This work was performed under the auspices of the U.S. Department of Energy, Division of Materials Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76CH00016.

## **References**

- [1] L.J. Oblonsky, A.J. Davenport, M.R. Ryan, H.S. Isaacs, R.C. Newman, *J. Electrochem. Soc.*, **144**, 2398 (1997).
- [2] C.S. Jeffcoate, H.S. Isaacs, A.J. Aldykiewicz, M.P. Ryan, *J. Electrochem. Soc.*, **147**, 540 (2000).
- [3] C.S. Jeffcoate, H.S. Isaacs, V. Laget, R. Buchheit, in *Mechanism of Al Alloy Corrosion and the Role of Chromate Inhibitors: Fourth Annual Report* (Ed. G.S. Frankel), p.193, Air Force Office of Scientific Research, Contract No. F49620-96-1-0479, (2000).



**Figure 1. Schematic of the electrochemical cell employed in the present study, showing the inflated position (a) where the chromate solution can react with the sample and the deflated position (b) where the reaction is paused.**