

# Chemical Study of Passivating Chromium Oxide Films by Soft X-ray Absorption Spectroscopy\*

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**Chromium oxide coatings deposited on stainless-steel surfaces were studied by X-ray absorption spectroscopy (XAS) using synchrotron radiation. Migration of manganese from the steel substrate into the film was found to be significant when  $\gamma$ -Cr<sub>2</sub>O<sub>3</sub> was developed by thermal treatment of an originally amorphous coating. The passivating efficiency of the film was then largely improved. The presence of other oxidation states of chromium was not confirmed by XAS.**

*Keywords: Passivating film; absorption spectroscopy; synchrotron radiation; chromium oxide*

## Introduction

Geiger-Müller radiation counters filled with a gas mixture containing a halogen are used as humidity probes for soils (Portuguese patent M. J. Carmezim, 86683, 1989), and are therefore subjected to severe corrosion conditions. With the purpose of developing a passivating coating over the cathodic surface of such counters, corrosion-resistant chromium oxide films deposited over stainless steel (Fe-Cr alloys) were obtained by chemical conversion and thermal treatment under a controlled H<sub>2</sub>-H<sub>2</sub>O atmosphere.<sup>1</sup>

The passivating efficiency was found to depend significantly on the structure type of the dominant oxide: trigonal ( $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>, corundum type) or cubic ( $\gamma$ -Cr<sub>2</sub>O<sub>3</sub>, defect spinel type). Bixbyite-type Cr<sub>2</sub>O<sub>3</sub> (also cubic) could eventually be formed but was not detected in X-ray diffraction (XRD) spectra of the oxide coatings.<sup>2</sup>

Nevertheless, some questions concerning the chemical nature of the films remained unsolved, namely, the possible presence of chromium in oxidation states other than 3+ when CrO<sub>3</sub> is the starting material, and the possibility of metal

diffusion from the substrate because the film thickness is only about 400–600 nm.<sup>3</sup> As both problems can be tackled by soft X-ray absorption spectroscopy (XAS), the oxygen 1s (K), and Cr, Fe, and Mn 2p (L<sub>2,3</sub>) absorption edges were studied using synchrotron radiation.

## Experimental

### Film Preparation

Samples of chromium oxide films deposited on cleaned surfaces of stainless-steel AISI 446 (Cr, 23–27; Mn, 2; and C, 0.2% m/m) were prepared<sup>1</sup> by chemical conversion with a solution of 300 g dm<sup>-3</sup> CrO<sub>3</sub> and 2.5 g dm<sup>-3</sup> sulfuric acid at 70 °C for 15 min.

After being washed with distilled water and dried in an oven, the samples were thermally treated under an H<sub>2</sub>-H<sub>2</sub>O atmosphere (dew points, -30 and -40 °C) at normal pressure for different times (5 and 15 min).<sup>1</sup>

### Film Characterization

The microstructures of the passivating oxide films were examined using scanning electron microscopy (SEM), and the crystallinity and phase constitution were monitored by XRD in a typical  $\theta/2\theta$  goniometer using Cu K $\alpha$  radiation *via* a graphite single-crystal monochromator.

The film thickness was in the range 400–600 nm, as measured directly by electron microscopy and later confirmed by indirect measurement through X-ray absorption using an X-ray fluorescence spectrometer.<sup>3</sup>

### X-ray Absorption Spectroscopy

Soft X-ray absorption was measured with an SX700(II) monochromator<sup>4</sup> [Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY)] and recorded in total electron-yield mode. The energy resolution was about 0.1 eV full width at half maximum (FWHM).

Samples were mounted on a plate and transferred to the ultra-high vacuum system where the pressure was kept in the

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$1.3 \times 10^{-8}$  Pa range while measurements were being taken. To check for oxygen contamination in the monochromator, the throughput of a copper foil was measured at the oxygen 1s absorption edge.

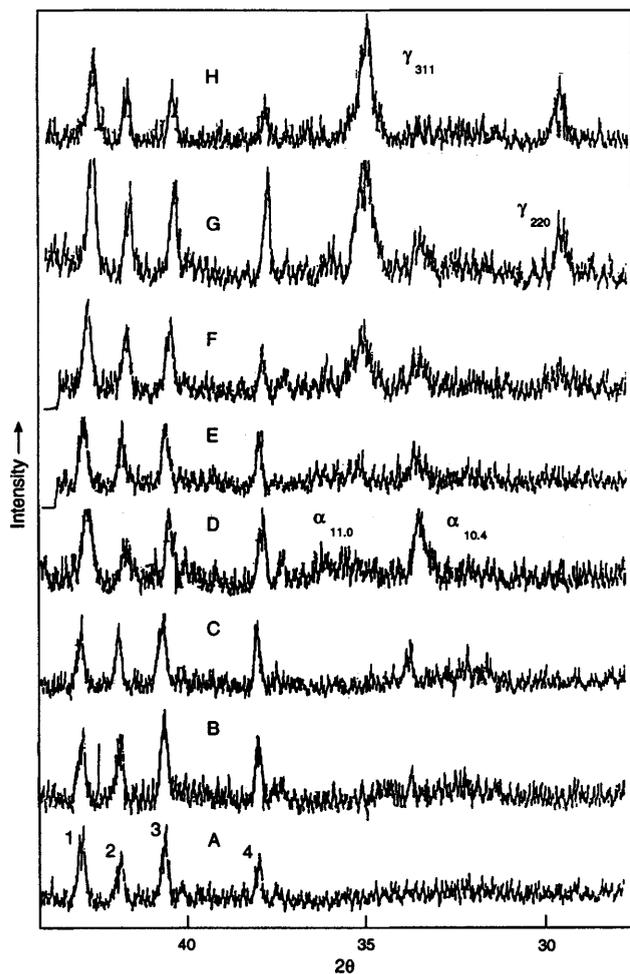
The energy calibration of the monochromator was performed by considering the 2p absorption edges of pure transition metals (Cr, Mn, and Fe) and using the energy-loss data of Fink *et al.*<sup>5</sup> as a reference. The calibration graph was linear in the probed energy range (400–800 eV).

### Results and Discussion

The passivating efficiency of the oxide coatings was clearly dependent on the microstructure and on the dominant  $\text{Cr}_2\text{O}_3$  structure types, features that are discussed in detail elsewhere.<sup>2</sup> Only aspects related to the oxidation state of chromium, and diffusion from the steel substrate will be accounted for here.

It is possible for oxide coatings to include amorphous and/or crystalline  $\text{Cr}_2\text{O}_3$ : the more common  $\alpha$  phase, trigonal, with the corundum structure type; a  $\gamma$  phase, cubic, defect spinel-type structure; and a bixbyite-type phase, also cubic.

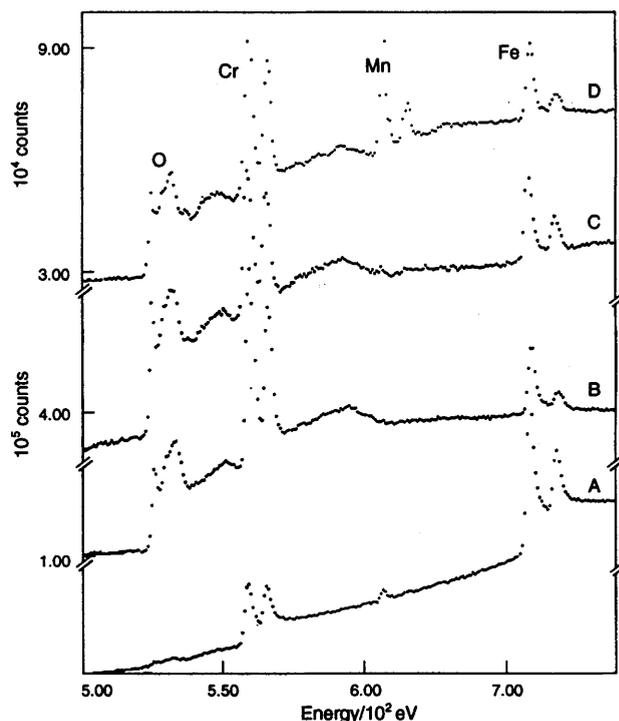
Fig. 1 shows the XRD data for A, the fresh stainless-steel surface (AISA 446); for B, an oxide coating prepared by



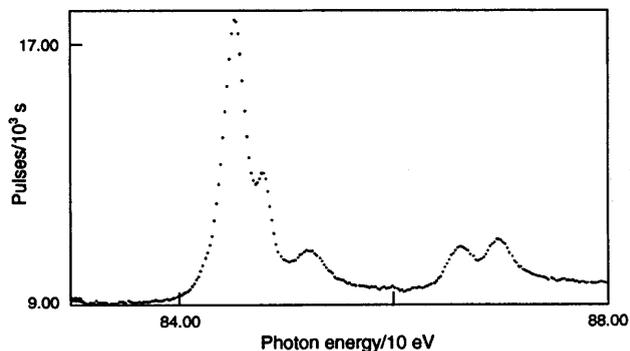
**Fig. 1** X-ray diffraction data: A, stainless steel (AISA 446); B, oxide coating prepared by chemical conversion; C, the same coating as in B, treated at 573 K for 5 min; D, oxide film treated at 973 K for 5 min; E, oxide film treated at 1073 K for 5 min; F, oxide film treated at 1073 K for 15 min; G, oxide film treated at 1173 K for 5 min; and H, oxide film treated at 1223 K for 5 min. 1–4, carbide lines in the stainless-steel substrate. Thermal treatments at dew point,  $-40^\circ\text{C}$

chemical conversion, and for C–H, various oxide films subjected to different thermal treatments under a  $\text{H}_2\text{--H}_2\text{O}$  atmosphere (dew point,  $-40^\circ\text{C}$ ) for 5 or 15 min. The presence of the crystalline trigonal phase ( $\alpha$  phase) in the original oxide coating (Fig. 1,B) is doubtful. Conversely, it starts to appear clearly at 573 K (Fig. 1,C). The onset temperature of the spinel-type  $\gamma$  phase is 1073 K (Fig. 1,F): the relative proportion of this phase increases with the treatment period, from 5 to 15 min, and also with temperature until the film at 1223 K (Fig. 1,H) contains a single oxide phase.

Fig. 2,A shows the broad X-ray absorption spectrum of a fresh stainless-steel surface: to ensure cleanliness the surface had been scraped with a ruby file under vacuum. In fact, no oxygen is detected with this spectrum. When Fig. 2,A is compared with the spectra of films in different structural states after various thermal treatments, it becomes apparent that there is diffusion from the metal substrate. Fig. 2,B shows that some iron has already diffused into the amorphous film; this iron remains regardless of the thermally induced structural



**Fig. 2** Broad X-ray absorption spectra for A, the stainless-steel substrate, B, amorphous chromium oxide, C, amorphous chromium oxide treated at 973 K, and D, amorphous chromium oxide treated at 1223 K



**Fig. 3** X-ray absorption-edge spectrum of the Mn 2p absorption edge for the oxide film treated at 1223 K (as for Fig. 1,H and Fig. 2,D)

evolution into  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> at 973 K under a H<sub>2</sub>-H<sub>2</sub>O atmosphere with a dew point of -40 °C (Fig. 2,C). This result is expected for the situation where iron(III) oxide is isostructural with  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>. Conversely, the diffusion of manganese is only detectable in the spectrum of the film subjected to thermal treatment at 1223 K (Fig. 2,D); here, the cubic defect spinel-type structure (Fig. 2,D) is dominant.

The L<sub>2,3</sub> absorption-edge spectrum of diffused manganese in the oxide film treated at 1223 K (Fig. 3) resembles closely that of the Mn<sup>2+</sup> X-ray absorption spectrum in a cubic crystal field.<sup>6</sup> This is consistent with the expected oxidation state of manganese in terms of crystal field stabilization energies (CFSEs) and site occupancies in a defect spinel-type structure

with approximate composition Cr<sub>2-x</sub>Mn<sub>x</sub>O<sub>3</sub>: no octahedral/tetrahedral site preference of Mn 3d<sup>5</sup> versus the high CFSE of Cr<sup>3+</sup> in octahedral coordination.

Additionally, the L<sub>2,3</sub> absorption-edge spectra of chromium in all the prepared films are identical (Fig. 4) and approach the X-ray absorption spectrum characteristics of Cr<sup>3+</sup> in a cubic crystal field.<sup>6</sup> No significant details were noticed that could indicate the presence of other chromium ion oxidation states, in particular, Cr<sup>6+</sup>, as previously argued.<sup>7</sup>

Work is in progress concerning the structural role of diffused ions from different substrates in relation to the properties of chromium oxide films obtained by chemical conversion.

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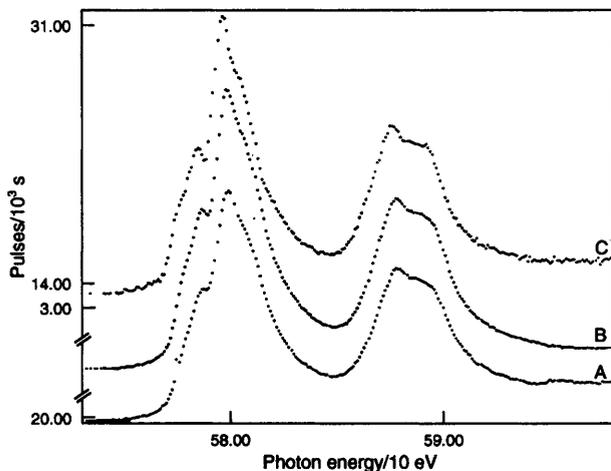


Fig. 4 X-ray absorption-edge spectra of Cr 2p: A, amorphous chromium oxide; B, amorphous chromium oxide treated at 973 K; and C, amorphous chromium oxide treated at 1123 K

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