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On the Formation of Cr(VI)-rich Chromate Conversion Coatings in Mechanically Damaged Areas on AA2024-T3

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Beamline(s): X10C

Introduction: Defects or mechanical damages in chromate conversion coatings (CCCs) are protected without further treatment by "self-healing" properties of the coating (1-3). "Self-healing" has been associated with migration of chromates to actively corroding sites (4-9). The formation of a protective Al(III)-Cr(VI) complex at damaged sites was first suggested by Abd Rabbo *et al.*(10). McCreery *et al.* later proposed and demonstrated the formation of an Al(III)-Cr(VI) complex in pits (5, 11). Earlier work from this laboratory has verified the presence of Al(III)-Cr(VI) complex in scratches (8, 9). In this work, we have performed a set of novel investigations to verify whether the hexavalent chromium content of the coating increases with the number of scratches on the AA2024-T3 substrate.

Methods and Materials: AA2024-T3 substrates were scratched in a controlled and systematic manner prior to the formation of CCCs using the Alodine 1200S® process. 1.0cm x 1.2cm area of the substrate was subjected to almost equidistant scratching in two mutually perpendicular directions. Samples with 5 x 5, 10 x 10, 20 x 20, 30 x 30, 40 x 40, 50 x 50 scratches were chromated. The ratio of Cr(VI)/Cr(Total) for each sample (triplicate) was determined using XANES. An unscratched sample was used as control.

Results: A conversion-coated sample is shown in figure 1. The Cr(VI)/Cr(Total), shown in figure 2, is seen to increase with the number of scratches on the substrate. A third order polynomial has been used to describe a relationship between the observed ratio of Cr(VI)/Cr(Total) to the total number of scratches on the substrate. Of various possible types of fit, the best fit was provided by the third order polynomial. A physical significance to the observed terms in the polynomial is currently being established. It appears to be very likely that the initial rise in the ratio is due to the formation of the Al(III)-Cr(VI) complex inside the scratches as expected. Mechanical damage leads to breakdown of the passive aluminum oxide film and hence promotes the much-needed dissolution of aluminum metal thereby helping accelerate the formation of the coating. This is analogous to the activity of the fluoride ions in breakdown of the oxide film. The later increase may be due to extensive breakdown of the film in a dendritic manner, thereby accelerating the metal dissolution not only at scratches but also at unscratched regions. Verification of the above mechanism is currently under progress.

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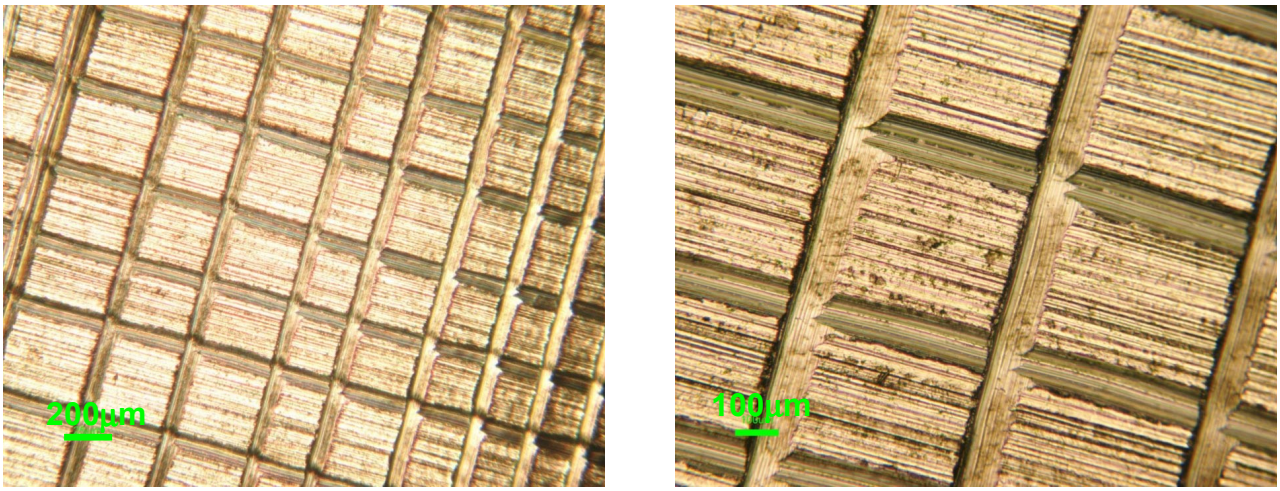

Fig 1: Digimicrograph of an AA2024-T3 sample with 30 scratches x 30 scratches in an area of 1.0 cm x 1.2 cm at two different magnifications.

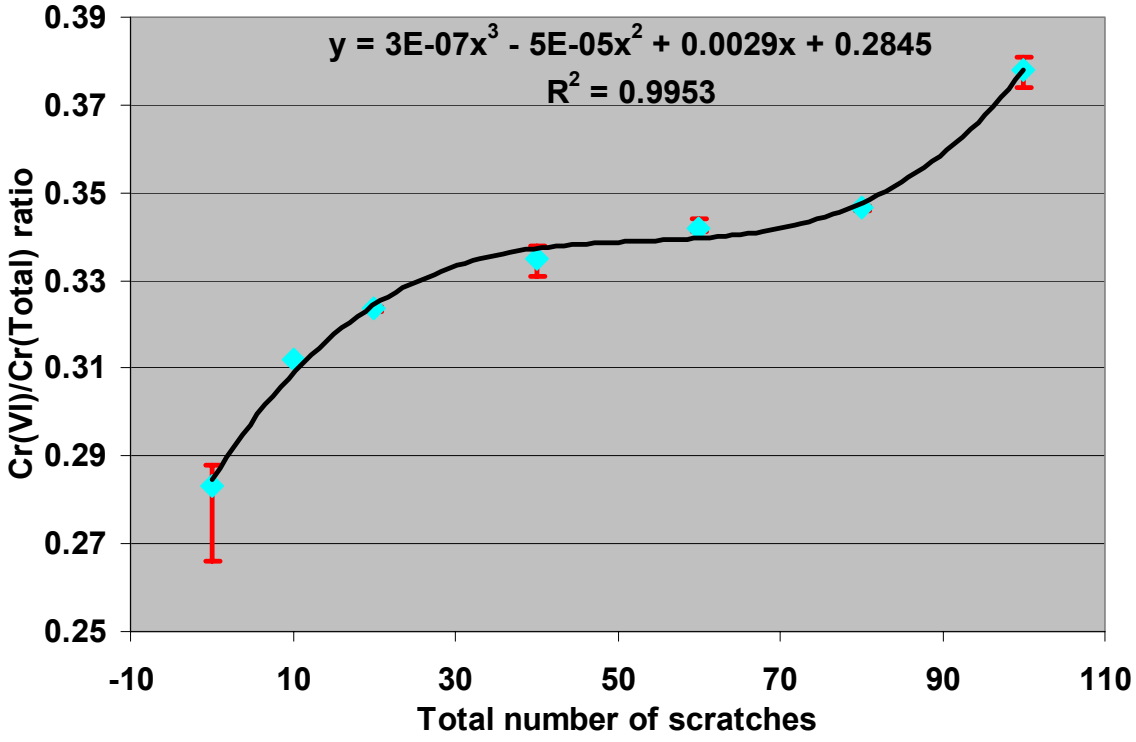

Fig 2: Graph showing the variation in ratio of Cr(VI)/Cr(Total) to the total number of scratches on the substrate.