

THERMAL STABILITY AND AGING CHARACTERISTICS OF CHROMATE CONVERSION COATINGS ON ALUMINUM ALLOY 2024-T3

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XANES and electrochemical impedance spectroscopies were used in parallel to correlate the amount of Cr(VI) in chromate conversion coatings (CCC) on Al 2024 and their corrosion resistance in order to understand the degradation mechanisms upon aging or heating. Cr(VI) species appear to be immobilized for temperatures higher than 80°C due to dehydration. CCC are shown to be dynamic in the first month of aging with no significant dehydration. Another degradation mechanism involving chemical changes is to be considered.

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Keywords: chromate, conversion coating, aluminum alloy 2024, corrosion resistance, XANES, heating effects, aging effects.

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 (0.1 to 2 μm) are used as stand-alone corrosion resistant coatings, and as pre-treatments for painting. CCCs 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. Active corrosion protection, also known as "self-healing", is a unique phenomenon exhibited by CCCs (1-4). It is thought to be related to a reservoir of labile Cr(VI) species (chromate or dichromate) located at the outer regions of the coating. Cr(VI) species can be released into the attacking solution and migrate to locally corroding areas to inhibit further damage. The inhibiting action involves reduction of Cr(VI) to insoluble Cr(III), which enables formation of a protective passive barrier film.

One of the key elements in the self-healing nature of CCCs is the stability and the mobility of the Cr(VI) reservoir. If this reservoir decomposes, or the release mechanism cannot be effective anymore, a major component of the corrosion resistance is lost. Gallacio et al. showed that loss of corrosion resistance occurs under salt fog testing at temperatures in excess of 75°C (5). At the same temperatures, they observed a dramatic decrease of the Cr(VI) amount released in corrosive solutions.

Effects of long term aging (> 24 hours) in ambient atmospheres at ambient temperatures are less clear but it is generally believed that corrosion resistance may also be lost (6, 7). Glass showed that the amount of Cr(VI) released in solution decreases by a factor of 10 in one month (8).

Understanding the mechanisms and kinetics of the corrosion protection degradation with time and temperature has practical implications for the application and use of the coatings. The relationship between dehydration of the CCCs and the decrease of the amount of Cr(VI) released in solution is now commonly acknowledged. An organic coating covering the CCC during aging (8) and heating (9) treatments has been shown to limit this decrease. Also, corrosion resistance is not lost for coatings heated up to 100°C in a steam chamber (5). Dehydration leads to formation of micro-cracks across the surface and it is generally believed that the whole amount of Cr(VI) species is reduced in the self-healing process, in order to repair the damage (7).

In this work, we report X-ray absorption near edge structure (XANES) determination of Cr(VI) content in the CCCs upon heating and aging treatments and evaluate its relationship with corrosion resistance. We show that other mechanisms linked with dehydration or chemical changes should be also taken into account.

EXPERIMENTAL

Coating Preparation. Panels of Al 2024-T3 (Cu 4.5%, Mg 1.5 % and Mn 0.6%) were cleaned in an alkaline bath (Na_2SiO_3 32 g/l, Na_2CO_3 48 g/l) at 65°C for 2 minutes, rinsed, deoxidized in a commercial Sanchem 1000 bath at 55°C for 3 minutes, rinsed and then finally treated in an Alodine 1200S chromating bath at room temperature for 1 to 3 minutes, rinsed and air-dried for 24 hours (hardening time). Alodine 1200S contains chromic acid (50-60%), fluoro salts (30-50 %) and $\text{K}_3\text{Fe}(\text{CN})_6$ as an accelerator (10-15%) (4, 10).

Heating treatments were carried out during 15 minutes up to 500°C. For the aging study, samples were left in ambient laboratory atmosphere (20-25°C, 30-50% RH) for times up to 2 months.

TGA/DTA. Thermal analysis was performed with a SEICO model 320 on powders freshly scraped from the panels (coating time = 20 minutes). Measurements were made from RT to 550°C under air (flow 100 ml/min) with a heating rate of 5°C/min.

X-ray Absorption Spectroscopy. XANES measurements at the Cr K edge ($E_0 = 5989$ eV) were made at the National Synchrotron Light Source on beam line X19A following well-established procedures (2, 11). The fluorescent intensity was recorded with a 13-element detector on samples tilted at 45° to the incident beam. Spectra were background subtracted and normalized so that the absorption coefficient, defined as fluorescent intensity over incident beam intensity is equal to 1 at $E = 6050$ eV. A good estimation of the ratio of Cr(VI) over total Cr is then directly given by the height of the pre-peak.

Corrosion Measurements. The coating corrosion resistance, R_c , was determined by electrochemical impedance spectroscopy (EIS) with a EG&G PAR 273 potentiostat coupled to a Solartron 1255 frequency response analyzer and Zplot software. Samples were left 24 hours in NaCl 0.5M before measurements. Panels were used as working electrodes whereas a platinum grid and a saturated calomel electrode were used as auxiliary and reference electrodes, respectively. The real and imaginary components of the impedance were recorded at the open circuit potential, using an a.c. perturbation of 10mV amplitude for frequencies ranging from 0.01 to 10000 Hz. R_c was deduced by

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integrating the imaginary component of the impedance (12). A good correlation is generally observed between EIS and salt spray testing (13-14).

Auger Electron Spectroscopy. AES was performed with a PHI-Perkin/Elmer 680 apparatus associated with Ar ion gun for depth profiles in order to get an estimation of the thickness and to follow the depth repartition of the elements C, O, Al (KLL peaks) and Cr (LMM peak) inside the coatings. The interface was defined as the moment when the aluminum metallic peak (at 1395 eV) dominated the oxide peak (at 1387 eV). Measurements were made with a 10kV 1nA electron beam, a sputtering rate of 27 nm/min and on sample areas without any cracks.

RESULTS AND DISCUSSION

Heating Study

Fig. 1 shows the TGA/DTA measurements made on CCC powders up to 550°C. The compound suffers a total weight loss of 48 % in three distinct steps in agreement with a previous report (15). A first endothermic process occurs at ca. 80°C, corresponding to the loss of water molecules (18% weight loss). The second process is strongly exothermic and occurs at 300°C. A noticeable odor of NH₃ and HCN was reported (15), suggesting the decomposition of the ferri/ferro-cyanide groups incorporated in the coating bath as accelerator. At 450°C, the third weight loss is observed, associated with an exothermic peak of variable intensity depending on sample. This transformation is referred in the literature as the onset of α -Cr₂O₃, also called "glow phenomenon"(16). It has been shown to be very sensitive to the chemical environment (16, 17).

The initial composition of the coating is often referred as a hydrated chromium oxide consisting, according to XPS results, in a variable mixture of Cr₂O₃.nH₂O, CrOOH or Cr(OH)₃ (7, 18, 19). Both Cr₂O₃.nH₂O and Cr(OH)₃ have been reported to decompose upon dehydration to a CrOOH intermediate form (20, 21). Loss of water is observed by condensation of the hydroxyl group in CrOOH at 250°C (21). This decomposition is a slightly endothermic process, very often hidden by more energetic transformations and thus is not observed in our measurements. CCCs are amorphous in the entire range of studied temperatures. The first X-ray diffraction diagram is obtained at 600°C, corresponding well to partially crystallized Cr₂O₃. Coating thickness measurements determined by AES profiles show a strong decrease up to 100°C and no significant variation after 100°C. A CCC with a coating time of one minute was measured varying from 350 nm to 200 nm during the dehydration process.

The correlation between the Cr(VI)/Cr ratio determined by XANES and the corrosion resistance is showed on Fig. 2 for CCCs on alloy 2024-T3. Regarding the variation of the curves, two zones of study may be defined, below or above a certain temperature of about 250°C, where clearly two behaviors are observed. This critical temperature may be associated with the second decomposition process observed in TGA/DTA at 300°C.

The Cr(VI)/Cr ratio does not show an abrupt decrease at 80°C, which might be expected to explain the decrease of Cr(VI) release in solution. Instead, it exhibits a slow

and progressive decrease from 32% to 20% up to 250°C, showing that a significant part of the chromate was reduced with temperature (a 10-12 % value is generally obtained for a pure Cr(III) compound (2)). The variation of the corrosion resistance is quite different; R_c decreases by two orders of magnitude at 80°C. It seems that the corrosion resistance value is strongly related with the release of the Cr(VI) species and hence the self-healing effect. Both are very low between 80 and 200°C whereas a relatively high amount of Cr(VI) (26 to 32 %) is still present inside the coating. This clearly shows that the reduction of the Cr(VI) species is not the main factor of the corrosion degradation. Cr(VI) species appear to be immobilized suggesting that chemical changes inside the coating due to moderately elevated temperature prevent their release.

The temperature at which those changes are observed corresponds to the first transformation measured by TGA, associated with dehydration. Water molecules could be directly involved in the mechanism of release of chromates in solution. A mechanism of release based on Raman spectroscopy and requiring water molecules to break covalent Cr(VI)-O-Cr(III) bonds has been suggested by McCreery et al (22). This would be in good agreement with previous works cited in the introduction, which show the importance of dehydration.

Above 250°C, the Cr(VI)/Cr ratio exhibits a strong increase and its value at 400°C is comparable to the one measured at room temperature. Clearly, a Cr(III) oxidation process is triggered. The corrosion resistance increases in parallel, showing a good correlation between the two parameters. After 450°C, most of the CCC decomposes to Cr_2O_3 and both Cr(VI) content and R_c decrease again.

The oxidation of Cr(III) to Cr(VI) or even possibly to intermediate valency such as IV or V, is a surface phenomenon well known from work on chromium-based catalysts (16, 20, 21, 23, 24). The exact nature of the intermediate compound has not been yet clearly established but it seems to depend on the Cr(III) starting compound and the chemical environment (25). Several works suggest that it could be a mixed valency (III and VI) oxide such as the chromium chromate $\text{Cr}_2(\text{CrO}_4)_3$ (21, 24). The mechanism of release of chromates is expected to be different (not requiring any water molecules) from the one existing at temperatures below 250°C. The Cr(VI) species are present at the surface of the coating and hence, could easily be released in the self-healing process.

The evolution of the corrosion resistance with temperature was also measured for a CCC on Al 1100 panels (99% Al, 1% Fe, Cu, Si) to assess any influence of the alloy composition on heating. The comparison with CCC on Al 2024 is shown Fig. 3. The corrosion resistance of coated Al 1100 panels does not decrease around 250°C, suggesting insensitivity to dehydration. R_c starts to decrease only after 300°C when the coating is tending towards its Cr(III) oxide final form. This stability may be only due to the fact that Al 1100 is much less sensitive to corrosion than Al 2024. Indeed, the high content of copper in Al 2024 enhances its strength but also its corrosion sensitivity by local galvanic action. Nevertheless, specific interaction between CCC and intermetallic particles in Al 2024 has been observed. CCC is not uniform all over the surface but thinner on the Cu-rich particles (26, 27). Hagans and Haas observed a strong presence of Fe on those particles suggesting the formation of a Cu-ferrocyanide complex (26). Regarding our results, CCC degradation may be also dependent of the alloy composition. The details of its mechanism are not yet resolved.

Aging Study

The same type of study was performed on samples aged in air to check their stability and determine whether the same mechanisms of degradation as those involved with moderately elevated temperatures were to be considered. XANES was performed on a sample aged for 5 months and the Cr(VI)/Cr ratio was measured to be 31 %. This value is very close to the one obtained on a fresh sample (32%), showing that no significant reduction of the chromates occurs upon aging. TGA/DTA was also performed on sample aged for two months and surprisingly, the total weight loss and the weight loss related to dehydration remain the same, respectively 48 % and 20 %. This would show that dehydration can not be the leading factor to explain the decrease of the amount of Cr(VI) released in solution in the first month of aging. Some of the hydroxide groups may decompose at lower temperatures, distorting the hydration rate measured by TGA. Although the plateau between the two weight loss events is less clear for an aged sample compared to a fresh one, the differential of the TGA (DTG) for the first weight loss remains very well centered around 80°C, suggesting that only water molecules from hydration are taken into account. Previous XPS study of the oxygen peak shows similar results: Kearns et al. did not observe any significant change in dehydration after 35 days, compared to a 24-hour old sample (28).

The evolution of the corrosion resistance on samples aged up to 2 months is shown Fig. 4 for two coating thicknesses. For a coating time of one minute, R_c decreases after 20 days from values between 2 and 3×10^6 to values in the order of 5×10^4 ohms.cm². No significant changes upon aging were observed for a coating time of 3 minutes. In this last case, the good stability of the corrosion resistance may be explained by the fact that a low but possibly sufficient Cr(VI) amount can be released in solution for the self-healing process. For thinner coatings, less chromate is available and its immobilization appears to result in the total loss of corrosion protection. More tests remain to be done to check this behavior.

Coating thickness measured by AES, exhibits a different evolution from that expected regarding the study with temperature : instead of decreasing, it increases markedly with time, indicating some chemical change inside the coating. A sample with a coating time of one minute was measured varying from 400 to 650 nm during the first month. Then the thickness remains steady between 600 and 650 nm. It is interesting to note that both the decrease of the Cr(VI) released in solution and the increase of the thickness occur in the first month (8). After this limit, both show little change. A correlation between the two parameters is to be considered, as if the chemical changes were responsible of the immobilization of the chromates. Those changes require further investigation. Among them, we observed by AES that the thickness of the inner layer where the Al-Cr mixed oxide is detected increased strongly, from 150 to 300 nm. Thus, an oxidation of metallic aluminum will explain partially the increase of the total thickness. Many important chemical and physical changes are observed during the first 24 hours of the coating life, which are also the setting and hardening time of the coating (28). The first month period could be a prolongation of those changes, on a smaller scale.

CONCLUSIONS

Reduction of Cr(VI) species has been observed between RT and 250°C. Nevertheless, our results show that it is not the main factor of degradation of the corrosion resistance above 80°C. Dehydration seems to cause immobilization of the chromates, which can not be released anymore in the "self-healing" process. Some influence of the alloy composition on the degradation mechanism has been observed but remains to be fully resolved.

No significant reduction of the Cr(VI) species or dehydration have been detected with time under ambient conditions. The immobilization of the Cr(VI) species due to chemical changes other than dehydration is to be considered. The increase of the thickness during the first month suggests that CCCs are still dynamic. Aluminum oxidation has been observed at the interface metal/coating. The mechanisms of chromates immobilization upon aging may be related to those changes but remain to be determined.

ACKNOWLEDGEMENTS

This work is supported by the Army Research Office and the Strategic Environmental Remediation 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.

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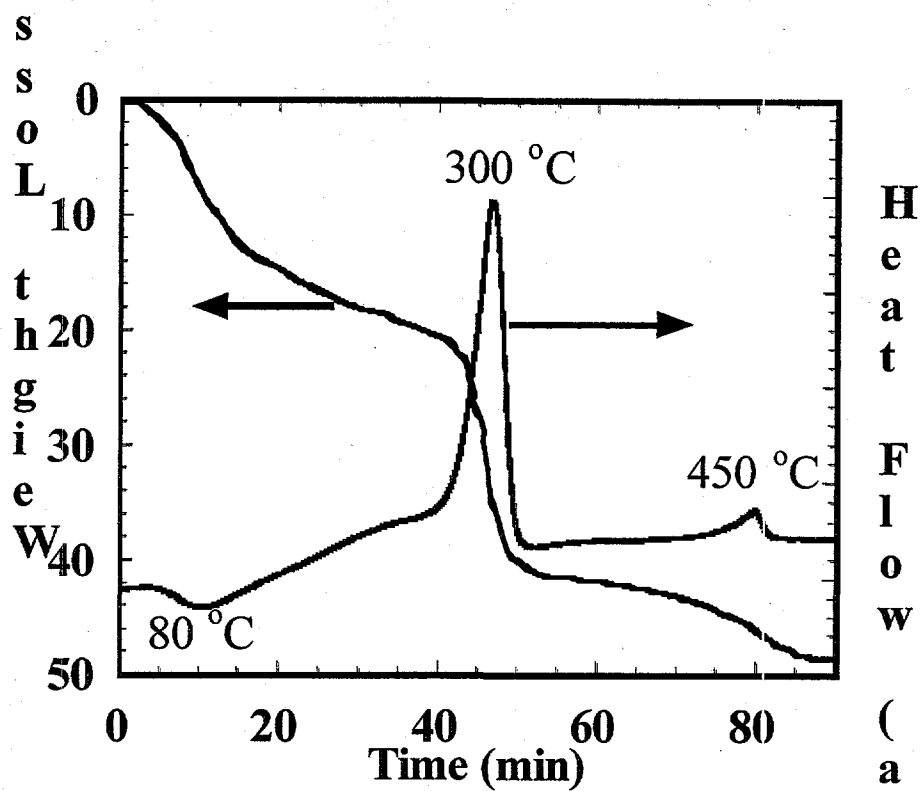


Figure 1: TGA and DTA measurements for Alodine 1200S chromate conversion coating on Al alloy 2024-T3 under its powder form (scraped from panel).

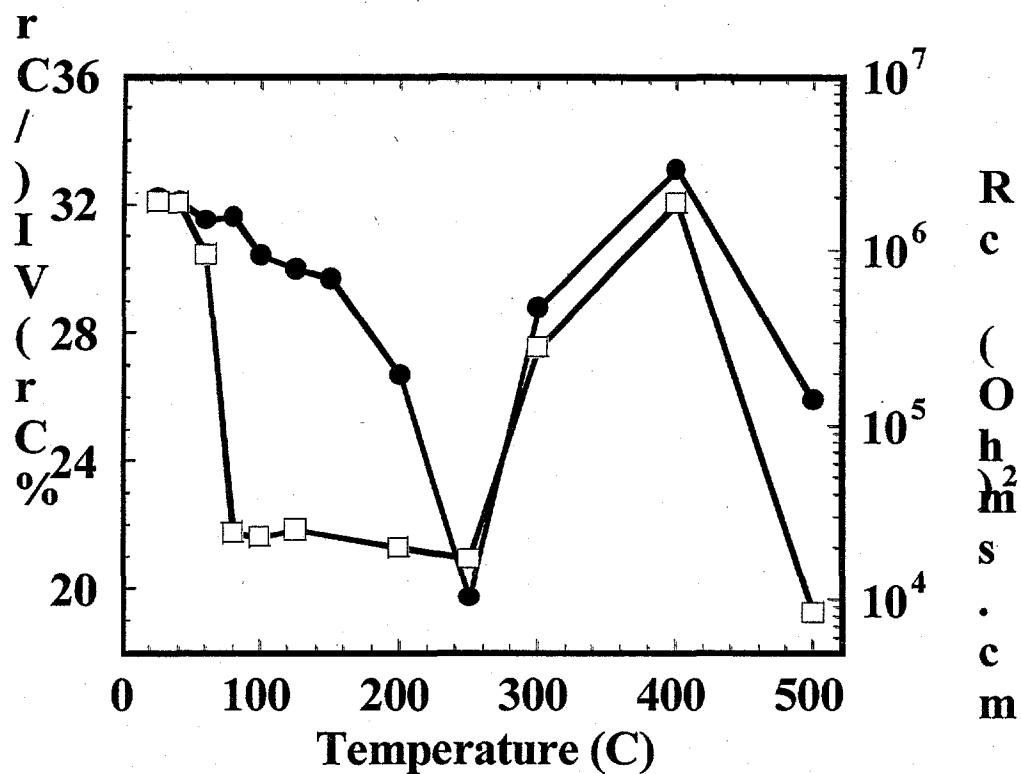


Figure 2: Evolution with temperature of the Cr(VI)/Cr ratio determined by XANES (●) and the corrosion resistance (●) for CCC on Al 2024 with 3 min coating time.

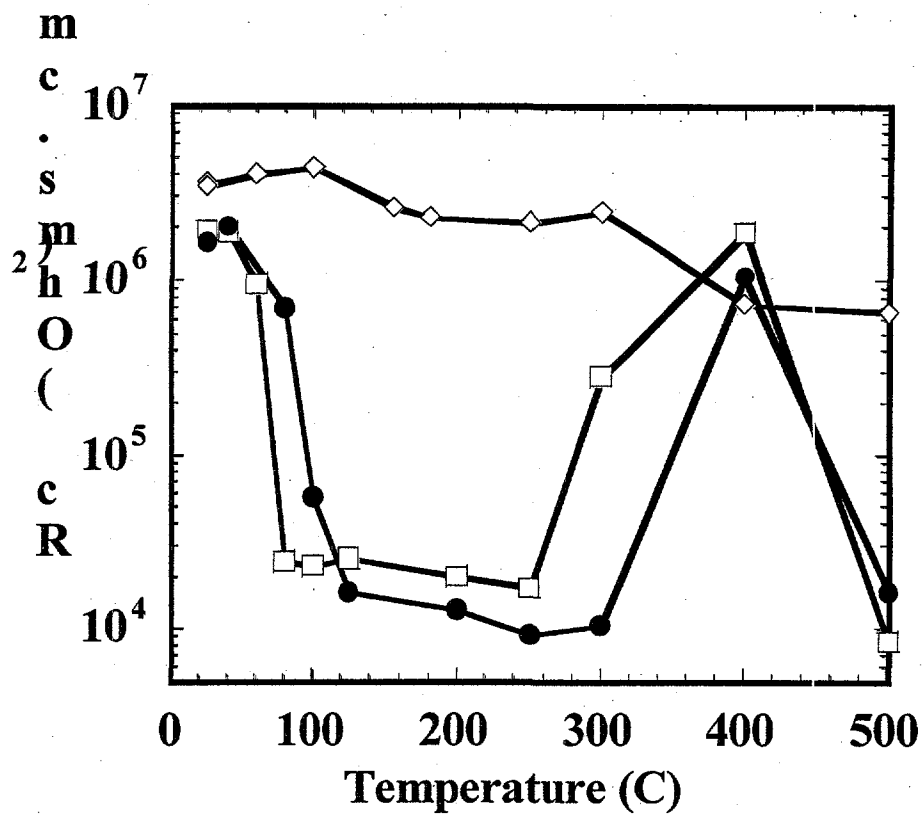


Figure 3: Evolution of the corrosion resistance for CCC on Al 2024, with respectively 1 min (●) and 3 min (●) coating time, on Al 1100 (*) with 3 min coating time.

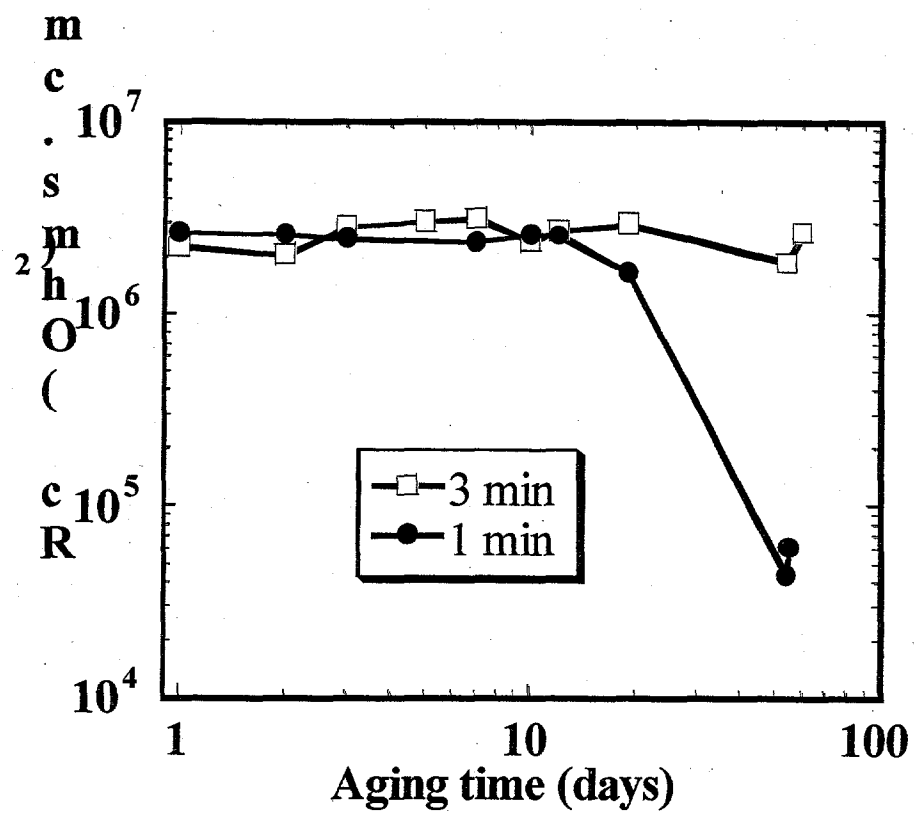


Figure 4: Evolution of the corrosion resistance with aging time for CCC on Al 2024 with 1 min (●) and 3 min (◻) coating time.