



Corrosion of cadmium plating by runway de-icing chemicals: Study of surface phenomena and comparison of corrosion tests

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ABSTRACT

In this paper, we study the corrosion of cadmium plating by four runway de-icing chemicals using electrochemical measurements and standard (immersion) and proposed (cyclic) runway de-icing corrosion tests for cadmium plating. Besides the obtained electrochemical and gravimetric data, we analyze the exposed surfaces by scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS) and infra-red spectroscopy (IR). The chemicals included in the tests are pure potassium formate, pure potassium acetate and the corresponding commercial chemicals.

Examinations revealed two parallel and linked phenomena on the plating surface, i.e., anodic dissolution of cadmium and development of corrosion products, primarily cadmium carbonate, CdCO_3 . Electrochemical measurements disclosed that the formed corrosion products slightly improved corrosion resistance of the surface but definitely did not stop corrosion completely, probably due to discontinuous structure. As for the studied de-icing chemicals, potassium formates systematically introduced more segmented corrosion products than potassium acetates and, subsequently, more severe corrosion on the specimens. Immersion cadmium corrosion test did not give very reliable results due to relatively low introduced corrosion rates and very large occasional scatter in the results. Cyclic cadmium corrosion tests introduced relatively greater corrosion rates and somewhat lower deviations than the immersion test, being hence, more reliable, but also more challenging in terms of meeting the weight change criteria for passing the test.

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1. Introduction

In aircraft, the use of light-weight alloys and composite materials shows an increasing trend. However, steel is still an essential material in some structural components, such as landing gears, where the combination of high tensile strength, stiffness and wear resistance is required [1,2]. Where applied, steel is often protected by an anodic coating, i.e., that of aluminum, zinc or cadmium, all of which exhibit a lower standard electrode potential than steel [3]. Indeed, cadmium plating may be considered as one of the primary corrosion protection measures for aircraft steel structures [4–6]. The corrosion protection ability of cadmium plating relies on, besides action as a sacrificial anode, a physical barrier effect and a good resistance to atmospheric attack, due to the tendency to form thermodynamically stable and insoluble corrosion products, typically cadmium hydroxides, chlorides or carbonates [3,4,7,8]. Although cadmium and zinc platings show many similarities in terms of deposition process and properties, cadmium plating is easier to solder and more protective in a salt fog environment [7,8]. However, cadmium and its vapors are toxic [7].

Therefore, more health- and eco-friendly alternatives to cadmium plating are currently sought [9–17]. Although the replacement of cadmium plating is a timely topic, it has to be recognized that such process is slow, particularly in aviation sector, with relatively long lifetime of the aircraft and prolonged standardization procedures for new coating processes.

At airfields, friction between the aircraft tires and the runway has to be high enough to enable safe operation. Since ice and snow decrease friction dramatically, runway de-icing measures have to be carried out during winter period in such areas where freezing conditions are possible, such as Northern countries. Besides mechanical removal of ice and snow, chemical de-icing may be employed. Today, runway de-icing chemicals are mainly based on potassium and sodium formates and corresponding acetates. However, the introduction of these chemicals in the market in mid-1990s was followed by a rise in the number of failed and damaged aircraft components. Particularly in the case of cadmium-plated steel components, either complete or partial loss of the cadmium plating has been frequently evidenced [5]. Although it is acknowledged that corrosion by runway de-icing chemicals is the probable reason for such deterioration of the cadmium plating, the mechanism by which corrosion proceeds is not clear.

In this paper, we examine the corrosion of cadmium plating by potassium formate and acetate based runway de-icing chemicals using several

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test methods, ranging from relatively fast few-hour electrochemical methods to relatively long cyclic tests that last up to a month. The research is unique in many aspects. Only few studies found in open literature report on the corrosion effects of runway de-icing chemicals on aircraft materials [18–20]. Further, where the corrosion behavior of cadmium-plated steel is reported, the surface is often covered by a further chromate passivation layer [16,18–20]. Here, the cadmium plating is not protected by the chromate layer, in order to reveal the fundamental behavior of the cadmium plating in the runway de-icing environment and to compare the results obtained by different corrosion tests. This paper also addresses the advantages and weak points of various cadmium corrosion tests, which may be used to, e.g., guide the development of test procedures.

2. Experimental

2.1. Materials

Bright-finished cadmium plating was applied on AISI 4130 steel specimens of the size of $25 \times 50 \times 1.7$ mm in accordance with the specification AMS-QQ-P-416 [21]. The plating and preceding specimen pre-treatment were performed by a subcontractor. A round suspension hole of 4 mm in diameter was cut in the specimens before the pre-treatment, which involved several steps: alkaline cleaning, rinsing with water, etching with sulfuric acid, rinsing with inhibited hydrochloric acid and then, finally, careful rinsing with water. Cadmium plating was then performed in a cadmium cyanide bath as per the specification AMS-QQ-P-416, followed by water rinsing. No post-plating chromate passivation treatment was performed on the coatings.

Corrosion tests were carried out using four de-icing chemicals, two of which were pure alkali metal salts and other two corresponding commercial products. Pure chemicals in the tests were potassium acetate (PAC) and potassium formate (PF), which were obtained as granules and as a 75 wt.% solution, respectively. These were then mixed with de-ionized water to prepare 50 wt.% solutions (that correspond to commercial chemicals in terms of salt concentration). Commercial potassium acetate based chemical, containing 50 wt.% potassium acetate, was received from Pirkkala Airport. In turn, commercial potassium formate based chemical, containing 50 wt.% potassium formate, was obtained from the airport of Vaasa. Both commercial products contained water as a solvent and 1–2% corrosion inhibitors. Measured pH values and oxygen contents for the chemicals are presented in Table 1.

2.2. Corrosion tests

Electrochemical measurements were performed as direct current dynamic polarization and alternating current electrochemical impedance spectroscopy (EIS) measurements. Polarization measurements were carried out by scanning the potential value from -0.8 to 1.2 V vs. E_{corr} at a rate of 0.5 mV/s. Electrochemical impedance measurements were performed by applying an alternating voltage of 10 mV in amplitude in the frequency range from 5 mHz to 100 MHz. In both measurements, a three-electrode cell containing the cadmium-plated steel working electrode, a platinum counter electrode and an Ag/AgCl (3.0 M KCl) reference electrode was employed. The cell was an EG&G Parc Flat Cell containing 300 ml of the electrolyte, i.e., the studied runway de-icing chemical. Before each type of electrochemical measurement,

the system was allowed to stabilize for 300 s, during which open circuit potential (OCP) was recorded. As EIS measurements were performed as a function of immersion time, the development of OCP could also be examined. Electrochemical measurements were accompanied by three corrosion tests designed to evaluate the corrosivity of runway de-icing chemicals towards cadmium-plated steel. Among these tests, a static immersion test followed a standard DIN VG97000 test, while the two cyclic tests followed AMS G-12 and Boeing test procedure suggestions.

In a standard DIN VG97000 test [22], two replicate cadmium-plated specimens, plated according to a Def-Stan 03-19 coating standard, are immersed in separate containers each containing 130 ± 5 ml of de-icing chemical. Immersion is carried out at 20 ± 2 °C for 168 h, i.e., for 7 days. Emphasis is put on pretreatment of the specimens before the tests: the specimens are first dipped for 25 ± 5 s in a 5 wt.% sodium dichromate solution at 65 ± 5 °C, then rinsed with running water and, finally, with warm (40 – 60 °C) water. Drying of the specimens is carried out in a furnace at 100 ± 2 °C for 30 min, followed by cooling in a desiccator containing freshly activated silica. The specimens are then weighed to the precision of 0.1 mg, tested and finally weighed again to the same precision. Here, cadmium plating of the specimens was carried out in accordance with AMS-QQ-P-416, to enable comparison between several tests. Furthermore, size of the specimens was the same as in all other tests, i.e., 25×50 mm ($1'' \times 2''$), instead of 25×75 mm that is suggested in the original test procedure. To facilitate reliable results, each test was carried out using three replicates instead of only two suggested by the standard.

AMS G-12 test [23] is a cyclic test the duration of which is 336 h, i.e., 14 days. The test begins on Friday with placing the containers, each containing 110 ± 10 ml of the studied de-icing chemical, in a heating chamber set to 32.2 ± 2.8 °C (90 ± 5 °F) and $30 \pm 5\%$ relative humidity. The exposure of acetone-wiped and weighed (to the precision of 0.1 mg) specimens to the de-icing chemical starts on Monday, the fourth test day, by immersion in the de-icing chemical for 24 ± 1 h. After the first (long) immersion, the specimens are immersed in the de-icing chemical every weekday for 90 ± 5 min. For the rest of the time, the specimens are placed in a heating chamber under the same conditions as the de-icing chemicals in the beginning of the test. Weighing of the exposed specimens is performed every Monday, Wednesday and Friday. Before weighing, exposed specimens are brushed carefully under de-ionized water with a soft brush using twelve strokes on both sides, followed by immersion into acetone for 10 s and then drying with a rag. Hence, cleaning and drying are only conducted before weighing the specimens, not after all immersions. In the tests of this study, all three replicate specimens were immersed in the same container involving 300 ml of de-icing chemical. This was due to a large amount of specimens in the tests, which would have made it impossible to fully control the immersion step. It is emphasized that care was taken that the specimens did not touch each other during the immersion, implying that galvanic corrosion between the specimens was impossible. The specimens were dried with a hair dryer instead of a rag that was instructed in the original test procedure. The reason was that some of the corrosion products that formed on the surfaces during some preliminary tests were evidently removed when wiping with a rag; this was not detected when drying was carried out with a hair dryer. Here, furthermore, the specimens were immersed the second last night in the de-icing chemical.

Boeing test [24] is also a cyclic test, but its duration is 744 h, i.e., 31 days. The test begins on Tuesday with an immersion of the methyl ethyl ketone-wiped and weighed (to the precision of 0.1 mg) specimens in the de-icing chemical for 48 ± 2 h. After this, the specimens are immersed in the de-icing chemical every weekday for 1.5 ± 0.5 h and, for the rest of the time, placed in a humidity chamber at the temperature of 18.4 ± 2.8 °C (65 ± 5 °F) and relative humidity of $40 \pm 10\%$. The specimens are weighed every Monday, Wednesday and Friday, starting from Friday the third test day. Again, similarly to

Table 1
Measured pH values and oxygen contents for the chemicals.

De-icing chemical	pH	Oxygen content, mg/l
Pure potassium formate	7.5	8.1
Commercial potassium formate	10.4	6.7
Pure potassium acetate	9.8	8.4
Commercial potassium acetate	10.7	8.6

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