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PROOF-OF-CONCEPT EXPERIMENT REPORT

FOCUSED ION BEAM STUDY OF CERIUM FILM FORMATION ON ALUMINIUM ALLOY 7075-T6

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Proof-of-Concept experiment details

Received sample:

The aluminium alloy (AA)7075-T6 in the form of 0.5 mm thick sheet with the nominal composition, in weight percent: 0.08 Si, 0.21 Fe, 1.67 Cu, 2.55 Mg, 5.81 Zn, 0.19 Cr, the remainder being Al, was received for FIB-SEM/EDXS characterisation. The sample was cut in the form of discs, diameter 10 mm.

The sample surface was abraded successively with 2,400- and 4,000-grit SiC emery papers and cleaned ultrasonically. Then they were immersed for various immersion times in corrosive media without and with different cerium salts: cerium(III) chloride $CeCl_3$, cerium(III) nitrate(V) $Ce(NO_3)_3$ and the cerium(III) acetate - $Ce(CH_3COO)_3$.

The sample names were:

- *Ground AA7075-T6*
- *AA7075-T6+$CeCl_3$*
- *AA7075-T6+$Ce(NO_3)_3$*
- *AA7075-T6+$Ce(OAc)_3$*

Planned analysis:

1st Imaging and microstructural characterisation of the ground and treated AA7075-T6 surface using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDXS). The analysed positions were marked with focused ion beam FIB-SEM (Pt deposition).

2rd The preparation of a lamella using FIB/SEM-FIB for scanning transmission electron microscopy (STEM) analysis.

Sample preparation:

The AA7075-T6 substrates were ground and immersed in a solution containing different Ce salts. The surface analyses were performed after various times of immersion (after 1 hour, 3 hours and 6 hours).

All analyses were performed within the framework of NANOREGION project, following the POC proposal submitted on 4/08/2020 and approved on 19/08/2020.

Measurement author, dates and place:

The sample preparation and the reported measurement have been performed by dr. Peter Rodič, Barbara Kapun and Bojan Ambrožič in the period from 20/08/20 to 7/10/20 at Nanocenter (Jamova cesta 39, Ljubljana). Analyses were performed with FEI Helios Nanolab 650 equipped with Oxford Instruments EDXS system with X-max SDD detector.

Preliminary measurements:

The ground alloy composition prior to and after the various time of immersion was analysed with FIB-SEM/EDXS.

Observation conditions:

Imaging: beam energy 3-15 KeV; secondary electron detector, backscattered electron detector.

The point, linear and mapping EDXS analyses have been performed with the following parameters: Beam energy: 3-15 KeV; probe current: ~1 nA.

The cross-section of selected regions on the sample was obtained after deposition of a thin layer of platinum on the surface (first 0.2 µm thick layer at 2 kV, 0.4 nA, second 1 µm thick layer deposited at 30 kV, 0.24 nA), followed by cutting the coating using Ga FIB beam at 30 kV, 9.4 nA. In the end, the surface was polished with Ga beam at 30 kV, 0.4 nA. Imaging along cross-section was performed by SEM using SEI mode at 5 kV energy. The EDXS mapping analysis of composition was obtained using EDXS Aztec software at 5-15 kV energy. Mapping of EDXS lasted for 1000s.

Main aim of the proposal:

The main aim was to determine alloy composition, initial corrosion in corrosive media and difference in the formation of the protective film in different cerium salts. Microstructural characterisation (the presence of intermetallic particles in the AA7075-T6 substrates) and the study of the Ce inhibitor/substrate mechanism was performed with SEM/EDSX. After various times of immersion (after 1 hour, 3 hours and 6 hours), the specimens were analysed by SEM/EDXS at the same positions in order to study the interaction of the Ce with the different intermetallic phases of the substrates vs time. Finally, the sample cross-section and STEM analysis was performed to determine the thickness of the formed cerium film and its morphology.

Results

1. The composition of ground AA7075-T6

In AA7075-T6, the main intermetallic Al_7Cu_2Fe and $(Al,Cu)_6(Fe,Cu)$ were observed and detected with SEM/EDXS (Figure 1). These intermetallic are seen as bright few micrometres large particles with various shape and size randomly spread in the aluminium matrix. Alloy also contains dispersed $MgZn_2$ (dark grey particles), which size is in the range of nanometres. According to literature, large particles are electrochemically less active than the matrix, and therefore they could lead to the dissolution of the surrounding areas. On the other hand, $MgZn_2$ is electrochemically more active than the matrix, and thus, they may lead to the intergranular corrosion of AA7075-T6.

Reference: Andreatta F, Terryn H, de Wit JH (2004) Corrosion behaviour of different tempers of AA7075 aluminium alloy. Electrochim Acta 49:2851–2862. doi:10.1016/j.electacta.2004.01.046

2. Film formation during immersion in various cerium salts

The SEM imaging of alloy surface prior and after immersion was studied. The corrosion products are seen on the alloy immersed in corrosive media sample AA7075-T6 after 6 hours of immersion. On the other hand, the formation of the nanometres thin cerium film is seen on samples AA7075-T6+$CeCl_3$, AA7075-T6+$Ce(NO_3)_3$ and AA7075-T6+$Ce(OAc)_3$. The thickness and structure are affected by the cerium salt. The thinner film was formed in $CeCl_3$ solution, therefore its presence was very difficult to detect. The film formed in $Ce(NO_3)_3$ is much thicker, but the formed cerium film does not evenly cover the surface. Such film has many pits and other defects. The most uniform film was formed in $Ce(OAc)_3$. From the obtained data, it can be concluded that the $Ce(OAc)_3$ is the most suitable candidate for efficient corrosion inhibition.

3. The morphology of the formed film during immersion in $Ce(OAc)_3$

The morphology of the formed film during immersion for 6 hours in $Ce(OAc)_3$ was additionally analysed. The thin film was noticed in the film formation on the intermetallic particles. The film is thicker and more compact on the intermetallic, and then become thinner and less compact in the surrounded aluminium matrix.

4. Cross-section and film thickness

The thickness of the formed film can be estimated to only a few nanometres. The film is present along the alloy surface. The EDXS mapping confirms the presence of O and Ce due to formation of CeO_2 film on the alloy surface. This approach finally gives more information about film thickness.

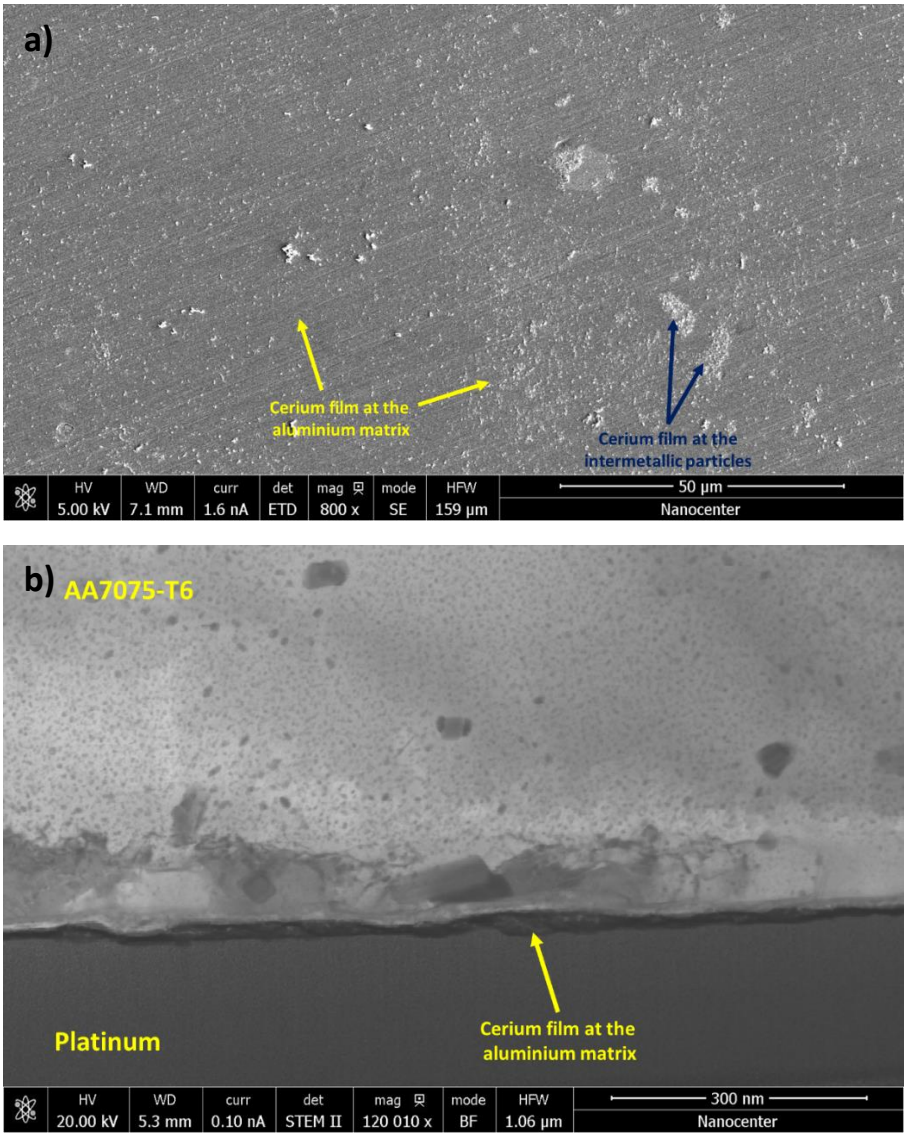

Figure 1: a) Surface appearance of AA7075-T6 immersed for 6 hours in NaCl + $Ce(OAc)_3$ solution, b) FIB cross-section of AA7075-T6 immersed for 6 hours in NaCl + $Ce(OAc)_3$ solution

Summary

The obtained results gave a better insight into the aluminium alloy composition and mechanism of corrosion inhibition/protection with cerium salts.

1) The structure of AA7075-T6 was heterogenous, where larger intermetallic present iron and copper-rich intermetallic. On the other hand, $MgZn_2$ nanometres particles were dispersed in the aluminium.

2) The formation of the inhibition film on the alloy surface was highly related to the used cerium salts, where $Ce(NO_3)_3$ and especially $Ce(OAc)_3$ form a thicker protective film on the surface. The most continuous film was formed in $Ce(OAc)_3$.

4) The cerium film formed from $Ce(OAc)_3$ was firstly formed on the larger intermetallic particles (catodic area). The film was thinner and more porous on the aluminium matrix.

5) The STEM analysis confirmed that the formed film is only few nanometres thick.

Final remarks on the effectiveness of the SEM/EDX investigations and FIB cross-sectioning for the study of protective coatings.

SEM/EDX investigations and FIB cross-sectioning have been proved to be effective in the study of the mechanism of corrosion inhibition/protection of the alloys with cerium salts and in the characterization of formed Ce film. These techniques are definitely suitable in providing essential information for the further development of protective coating systems.

This report has been written by **dr. Peter Rodič** and **dr. Bojan Ambrožič** (Ljubljana, 15 November 2021)