

## SEM & EDS determination of the impact of inhibitor containing corrosive media over the AA2024 superficial morphology

E. Matter, S. Kozhukharov, M. Machkova

**Abstract:** *The corrosion processes could be considered as destruction of the solids (especially metals and alloys) due to their interactions with the surrounding environment. Undoubtedly, the corrosion of the metals and alloys, and all related chemical and electrochemical processes possess entirely heterogeneous nature. In that means, the metal surface is interface where these processes occur. Consequently, the impact of the corrosion, together with the activity of the corrosion inhibitors could be determined by SEM observations of the surface after prolonged exposition in the respective inhibitor containing model corrosive media.*

**Key words:** SEM observations, Ce-compounds, AA2024 alloy, superficial morphology

### INTRODUCTION

Generally, the Al – Cu alloys, such as AA2024 are susceptible to localised corrosion [1, 2]. Their enhanced susceptibility is originated from the appearance superficial galvanic couples, when the alloy is in contact with chloride solution. At this condition, between the basic metal and the alloying elements a potential difference arises, resulting to appearance of cathodic and anodic areas. Due to the limited solubility of Cu in Al, it forms precipitates, during the metallurgic production. These intermetallic precipitates are the preferable centres, of formation of galvanic couples, and consequently – predominant locations for localised corrosion attack. The mechanism of the pitting corrosion and its inhibition by lanthanide compounds are described in detail in the literature [3 – 5]. According to Yasakau [3] the most spread intermetallic is so called “S-phase”, composed by  $Al_2CuMg$ . In these particles, after dissolution of Mg, the Cu remnants becomes be cathodes, causing electrochemical dissolution of Al, initially inside the S-phase particle, and afterwards, in its surrounds. In addition, Srinivasa [5] mentions that there are other less active, fine precipitates, as well. Furthermore, in the same review, the kinetics of nucleation and posterior growth of the corrosion pits is described in detail. Thus, three basic stages are emphasised: pit initiation, metastable pitting, and at last, a stable pitting growth.

On the other hand, the mechanism of corrosion inhibition by Ce-salts is described to be result of precipitation of Ce-oxides/hydroxides as derivatives of Cerium ions and the  $OH^-$  anions as products of the oxygen reduction on the cathodic sides. As result, the Ce ions form island-like precipitates, which cover predominantly the cathodic areas. Taking in account that all processes pass on the metallic surface, the correlation between approach, applied for preliminary treatment and the corrosion impact is also described in previous works [6].

The purpose of the present research work is to elucidate the influence of the anionic moieties, as well as the oxidation state of the cerium ions of several Ce-salts, as potential corrosion inhibitors for AA2024 by superficial morphological observations

### EXPERIMENTAL

**Materials and methods** specimens of AA2024 with equal sizes were exposed for 25 days to model corrosive media, composed by 0.01M NaCl solutions, each one with  $5 \times 10^{-5}M$  addition of the respective cerium salt. The corresponding salts selected were as follows: Cerous nitrate –  $Ce(NO_3)_3$ ; Cerous chloride –  $CeCl_3$ ; Diammonium Pentanitrocerate  $(NH_4)_2Ce(NO_3)_5$  and cerous sulphate  $Ce_2(SO_4)_3$  For better completeness, experiments with three of the respective ceric salts:  $Ce(NO_3)_4$ ;  $(NH_4)_2Ce(NO_3)_6$   $Ce(SO_4)_2$  also were performed

**Sample preparation** – The samples were preliminary treated, following the prescription for mechanical treatment procedure, as is described in previous works [2, 6].

**SEM observations and EDS analyses** –they were performed using Scanning Electronic Microscopy (SEM), (TESCAN, SEM/FIB LYRA I XMU). Local compositions and map data analyses were performed by Energy Dispersion Spectroscopy (EDS), (Quantax 200 of BRUKER detector) which is attached to the SEM equipment.

## RESULTS AND DISCUSSIONS

### Cerous inhibitors

**SEM Observations:** After 25 days of exposure of the respective AA2024 samples, the differences among the inhibitor's mechanisms become obvious.

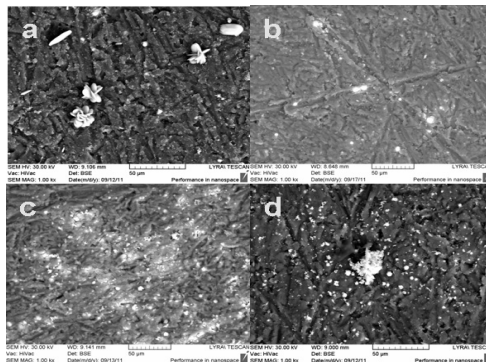


Fig. 1. Comparison among SEM superficial images after 25 days of exposure of AA2024 in solution with:  $\text{Ce}(\text{NO}_3)_3$  - a,  $\text{CeCl}_3$  - b,  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_5$  - c and  $\text{Ce}_2(\text{SO}_4)_3$  - d

Figure 1 undoubtedly evinces that there is a remarkable difference among the Ce-precipitates, as consequence of the use of different Ce-compounds as corrosion inhibitors. This difference reveals that the respective precipitates are formed by completely different mechanisms. Compared to all rest Ce-inhibitors, clearly distinguishable singular crystals on the most active cathodic zones Ce-oxides/hydroxides are formed, when  $\text{Ce}(\text{NO}_3)_3$  is added to the corrosive medium. These crystals are accompanied by very small precipitates. In comparison, the addition of  $\text{CeCl}_3$  leads to much more uniform distribution of the Ce-precipitates. In contrary to all rest cases,  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_5$  leads to formation of larger number of small precipitate islands, connected by almost continuous white layer. The sediments obtained from  $\text{Ce}_2(\text{SO}_4)_3$ , are relatively similar to these of  $\text{Ce}(\text{NO}_3)_3$ , but in that case, they are amorphous. In both cases (a, and d), the presence of large sized precipitates should be consequence of a larger duration of their growth. Consequently, these large size objects were constantly supplied by new quantities of Ce-ions, at the appropriated pH (i.e.  $\text{OH}^-$  ions) for their growth. By other words, these precipitates do not form any dense barrier, able to block the pits under them. As result, the permanent growth of Ce-sediments coincides with continuous development of the respective corrosion pits, under them.

In contrary,  $\text{CeCl}_3$  (b), and  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_5$  (c) have relatively equal size distribution. In addition, they are rather smaller, compared to the large islands discussed above. This fact indicates that the pitting growth is completely interrupted by formation of dense coverage. Particularly, in the case of  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_5$ , the presence of white layer could be explained, considering the probable re-deposition of copper particles, originated from the remnants of the S-phases. However, such assumption does not look reliable enough. The copper re-deposition arises at later stages of the pitting corrosion, and in presence of

whatever Ce-precipitates, such process looks almost impossible. Much more probable consideration looks that after the blocking of the most active S-phases, the rest cathodic sides become the main pitting centres. Taking in account this model for subsequent coverage of the cathodic zones, by Ce-precipitates, the description of the differences among the corresponding Ce-inhibitors could be summarized as follows:

The pitting growth is hindered even at its initial stage in the cases of  $\text{CeCl}_3$  - (b), and  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_5$  - (c), whereas for  $\text{Ce}(\text{NO}_3)_3$  – (a), and  $\text{Ce}_2(\text{SO}_4)_3$  – (d), it seems that the Ce-precipitate depositions do not form enough dense barrier to the access of corrosive species to the pitting centres.

More detailed comparative analysis of positions (a) and (d) discovers that besides the aptitudes of the respective Ce-precipitates from  $\text{Ce}(\text{NO}_3)_3$ , and  $\text{Ce}_2(\text{SO}_4)_3$  to form either crystalline, or amorphous large agglomerates, the smaller aggregates around them possess different number. The lower number of small precipitates in the former case indicates that the nitrate ions retard the precipitation of Ce-oxides/hydroxides. Thus, the crystals appear at later stage as result of slow gradual growth while in the case of  $\text{Ce}_2(\text{SO}_4)_3$ , the sediments are in form of agglomerated structures, composed by smaller aggregates. They are surrounded by large number of small sized precipitates, indicating that the large sized agglomerates appear at earlier stages of the pitting formation, and on the most active intermetallics. In that case, becomes clear that these agglomerates possess enough low density which enables access of corrosive species (as various ions from the electrolyte and dissolved  $\text{O}_2$ ). In the case of  $\text{Ce}(\text{NO}_3)_3$  the crystals look to be rather dense. Taking in account that they appear at later stage, the rate of their gradual growth is not enough high to hinder the development of the corrosion pits under them. Even after covering of the entire active zone, the respective crystal could entrap ions from the electrolyte in the zone of the pitting spot. Similar phenomenon is observed in cases of coatings, where corrosive ions penetrate through the coating, and afterwards they remain enclosed under the coating. That phenomenon is known as “blistering”.

**EDS measurements:** Generally, all of the white island-like precipitates have revealed high content of cerium. The maps analyses for distribution of the elements are represented in figure 2.

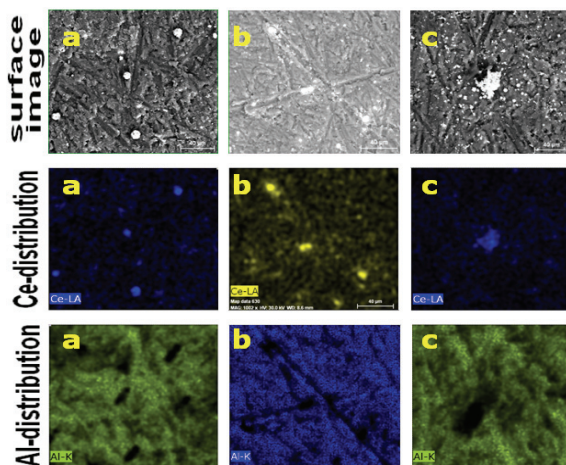


Fig. 2. EDS – map analyses of AA2024 specimens after 25 days exposure in solution with:  $\text{Ce}(\text{NO}_3)_3$ – a,  $\text{CeCl}_3$  – b, and  $\text{Ce}_2(\text{SO}_4)_3$  - d

The figure obviously reveals that the white coloured precipitates belong to Ce – oxides/hydroxides for the nitrate, chloride and the sulphate solutions. Regarding the diammonium pentanitrocerate  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_5$  it was established that the white sediments

are rather represented by mixture of Ce-precipitates, with involved aluminum containing corrosion products. Taking in account that this Ce-salt is a complex compound, and in addition, the ammonium ions possess aptitude to form complexes, it could be concluded that they are able to promote co-precipitation of Ce – oxides/hydroxides, with Al – corrosion products. In a previous work [2] was mentioned that the aluminium dissolution could pass through several stages:  $Al^0 \rightarrow Al^{3+} \rightarrow Al(OH)Cl_2 \rightarrow Al(OH)_2Cl \rightarrow Al(OH)_3$ . That fact confirms the assumption that the  $NH_4^+$  ions interact with the intermediated Al – hydrochlorides, and form precipitates, with better adhesion to the metal surface. Here, should be mentioned that all of the samples passed vigorous cleaning, and the  $Al(OH)_3$  were removed from their surfaces. That is the reason for absence of whatever white layer in the rest cases. In addition, the discussed above white layer is formed predominantly around the Ce-precipitates, which shows that the Ce-oxides/hydroxides are the reason for the better adhesion of the aluminum containing precipitates.

Indeed, the point analysis revealed simultaneous presence of aluminium and cerium in the precipitates, as is shown in figure 3. The presence of other elements there (Fe, Cu, and Mg) is originated by the inermetallics, because they are centers of corrosion, and consequently – inhibitor’s precipitation.

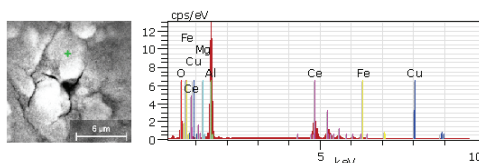


Fig. 3. EDS – point analysis of of AA2024 specimen after 25 days exposure in  $(NH_4)_2Ce(NO_3)_6$  containing solution

In contrary, the line analysis performed for the case of  $Ce(NO_3)_3$ , reveals that the regions of increase of Ce – content, overlap the decrease of Al. In addition, exactly these regions are the locations of the clearly formed crystals, as could be seen from the figure below:

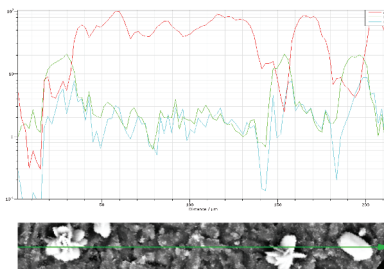


Fig. 4. EDS – line analysis of of AA2024 specimen after 25 days exposure in  $(NH_4)_2Ce(NO_3)_6$  containing solution

This figure reveals that the crystalline structures observed for the case of cerium nitrate are entirely composed by Ce-precipitates, and do not contain any  $Al(OH)_3$  corrosion products. The coincident differences between the structures and compositions of the precipitates of  $(NH_4)_2Ce(NO_3)_6$  and  $Ce(NO_3)_3$ , are undoubted indications for differences between the respective precipitation mechanisms. Consequently, the anionic parts of the cerium salts play significant role for the mechanism and kinetics of the Ce-precipitation.

### Ceric inhibitors

After 25 days all three Ce(IV) inhibitors reveal uniform layers of corrosion products, and their superficial morphologies are completely different from the previous group. While for the former two inhibitors (Fig. 5, positions a, and b), shapeless porous sponge-like films are formed, the last one (position c), leads to a film which repeats the metal surface and possesses a “dry land” cracked structure.

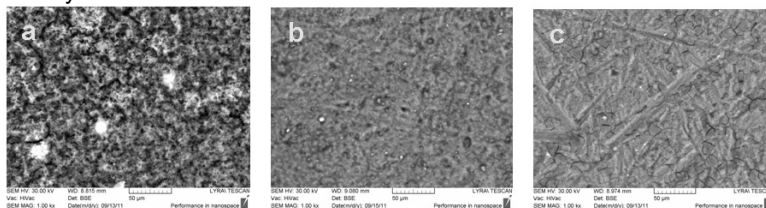


Fig. 5. SEM superficial images after 25 days of exposure of AA2024 in solution with:  $\text{Ce}(\text{NO}_3)_4$ – a,  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  – b and  $\text{Ce}(\text{SO}_4)_2$  - c

### CONCLUSIONS

There is a remarkable difference among the Ce-precipitates, as consequence of the use of different Ce-compounds as corrosion inhibitors. This difference reveals that the respective precipitates are formed by completely different mechanisms. For both of  $\text{Ce}(\text{NO}_3)_3$  and  $\text{Ce}_2(\text{SO}_4)_3$  simultaneous presence of definitely large and small deposits is observable, whereas for  $\text{CeCl}_3$  and  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_5$  the precipitates possess relatively equal sizes. Probably the latter form dense barriers, which efficiently stop the pitting growth, while at the former the corrosion pits continue to growth even under the Ce-sediments. In the case of  $\text{Ce}(\text{NO}_3)_3$  a larger time is necessary for growth of the respective crystalline structures, while the precipitates of  $\text{Ce}_2(\text{SO}_4)_3$  are just not dense.

In the case of  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_5$  a white layer of corrosion products was observed, which means that the  $\text{NH}_4^+$  ions interacts with the intermediated Al – hydrochlorides, and forms precipitates, with better adhesion to the metal surface.

All three Ce(IV) inhibitors reveal layers of corrosion products, and their superficial morphologies are completely different from the respective Ce(III) compounds.

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Докладът е рецензиран