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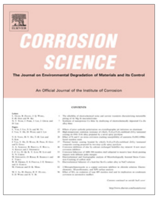

A localized approach to study the effect of cerium salts as cathodic inhibitor on iron/aluminum galvanic coupling

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ABSTRACT

The inhibition effect of cerium salts on iron/aluminum galvanic coupling was investigated by electrochemical microcell and Scanning Vibrating Electrochemical Technique (SVET). The importance of the electrode geometry on the SVET responses was evidenced. The effect of concentration and the influence of the anionic part of cerium salts on the inhibitive efficiencies and protective mechanisms were studied. Cerium salts inhibit the corrosion of iron/aluminum galvanic coupling by reducing the cathodic activity. Microcell analysis confirmed the passivation of aluminum. (SEM + EDS) analyses allowed to understand how the cerium salts act to improve the corrosion behavior.

1. Introduction

One of the ways to protect AA2024 (used in aerospace industry for its mechanical properties) against corrosion is to clad it with AA1050 [1–3]. However, AA1050 considered as pure aluminum contains some iron-rich intermetallics, with and without silicon (Al_3Fe and α-AlFeSi) [4–7]. Therefore, AA1050 even is less sensitive to corrosion than AA2024 can present some susceptibility to corrosion attack when exposed to a corrosive medium [1]. Indeed, iron-rich intermetallics (Al_3Fe, α-AlFeSi) are nobler than the aluminum matrix [6,7]. Consequently, in a neutral solution, the cathodic reaction occurs on the iron-rich intermetallics and the oxidation reaction corresponds to the dissolution of the matrix [8–12].

$$Al \rightarrow Al^{3+} + 3e^- \qquad (1)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (2)$$

In order to prevent the corrosion of aluminum alloys, many studies are carried out by using cerium salts. They are considered as environmentally friendly and also as a credible alternative to the use of the hexavalent chromate inhibitors [13–20].

The scanning vibrating electrode technique (SVET) is an electrochemical method which is able to resolve and quantify localized corrosion [21,22]. The SVET has found a wide range of applications by following the corrosion process occurring at the active sites (cathodic and anodic zones, pores or defects). SVET gives information on the flow of charged species (ionic currents) without identifying their chemical nature. It measures local potential changes in solution that are related to ionic currents generated by the corrosion activity of specimens in aqueous medium [23]. By comparing the current values, the efficiency of inhibitors can be analyzed. Using SVET technique, Aldykiewicz et al. showed the efficiency of cerium chloride as corrosion inhibitor for aluminum–copper alloy. They observed the decrease in the current supplied to the anodic reaction thereby reducing the rate of aluminum dissolution [24]. However, Ogle et al. by applying localized electrochemical techniques to cut edge corrosion noticed that the efficiency of chemical inhibition is highly dependent on the chemical and electrochemical environments which are found in the vicinity of the cut edge [25]. The strong galvanic couple set up between the steel and the zinc leads to large electrical field variations, and the close proximity of the anodic and cathodic reactions to significant changes in the chemical environment including increases in $[OH^-]$ and $[Zn^{2+}]$. This means in the case of aluminum alloys and in the presence of cerium salts that the galvanic coupling between the intermetallics and the matrix (aluminum) accelerates the dissolution of Al^{3+} ions and induces an increase in $[OH^-]$ leading to the precipitation of hydroxides or oxides of cerium according to Eq. (3) [10–12,26].

$$Ce^{3+} + 3OH^- \rightarrow Ce(OH)_3 \rightarrow CeO_2 + H_3O^+ + e^- \qquad (3)$$

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Consequently, the chemical nature of cerium salts (oxidation state, anionic part, etc.) and their concentration may also play a major role in inhibiting effect of the corrosion of aluminum alloys [27–30]. Nevertheless, investigations by using localized electrochemical techniques need to be performed in order to better understand the inhibition mechanism, deposition kinetics of cerium salts and their efficiency, especially for AA1050. Elsewhere, Bastos et al. also investigated the efficiency of corrosion inhibitors by SVET [31]. The inhibition efficiency was evidenced by analyzing the current of the sample in the presence and absence of corrosion inhibitors. They reported that in optimal conditions, SVET can allow to investigate with accuracy inhibition efficiency of corrosion inhibitors. Thus, in order to conduct SVET measurements accurately, some authors tested several parameters to obtain the optimal conditions, such as the height of the probe tip [32], the conductivity of the electrolyte [33,34], the inclination of the probe tip [35]. Akid et al. investigated the calibration procedure to evaluate the optimum operating parameters for maximum signal detection of point source activity [36]. McMurray et al. demonstrated that a large amplitude vibration can induce artifacts in localized corrosion [37]. However, no study has been reported with the SVET (to our knowledge) in the case of a galvanic coupling by studying the effect of the electrode geometry on the SVET response, on the other hand, by keeping constant the shape and size of one electrode such as the cathode and changing the shape and size of the anode. Studies need to be conducted to fill this lack.

The electrochemical micro-cell is a well-established method for the study of the electrochemical behavior of intermetallic compounds in aluminum alloys [7,8,38–42]. The application of this technique for the study of inhibition processes in aluminum alloys is a rather new approach. Ralston et al. and Birbilis et al. investigated the behavior of intermetallics in AA2024-T3 exposed to aqueous vanadate solutions [43,44]. Paussa et al. employed the micro-cell for the in situ investigation of intermetallics in AA2024-T3 after exposure to aqueous solutions containing cerium salts [45]. Andreatta et al. recently investigated by electrochemical micro-cell AA2024 cladded with AA1050 after immersion in cerium chloride solutions. Characterization by micro-cell indicated that the overall electrochemical behavior was improved by the cerium deposition. The breakdown potential in potentiodynamic polarization curves becomes more positive due to the cerium deposition both on the areas containing Fe-rich intermetallics and on the matrix.

The aim of this work is to study the inhibitory effect of cerium salts on the iron–aluminum galvanic coupling characteristic of AA1050. Several electrode geometries were tested to find the suited electrode geometry for SVET tests. With the suited electrode geometry, the parameters affecting the efficiency of cerium salts as corrosion inhibitors for iron–aluminum alloys were investigated and discussed. For one electrode geometry, the electrochemical microcell technique was used to study the passivation of aluminum in the absence and in the presence of cerium salt.

2. Experimental

To investigate the inhibitory effect of cerium salts, four electrode models with different geometries were fabricated by inserting a low carbon steel rod of 2 mm in diameter in the center of pure aluminum (purity 99.5%) of different shapes (Fig. 1(a)–(c)) and one working electrode consisted by two rods of low carbon steel and pure aluminum (Fig. 1(d)). To note that, for the electrode models 1(a) and 1(b), the pure aluminum was drilled in its center and a rod low carbon steel was introduced by force into the hole. The assembly of the two materials gave a perfectly joined interface, avoiding any crevice corrosion due to surface defects.

(1) Working electrode 1: The rod of low carbon steel of 2 mm in diameter was inserted in a pure aluminum of 6.5 mm in diameter and then embedded in an epoxy resin. The surface area ratio Fe/Al is about 1/10. This kind of working electrode (in surface area ratio) is usually used to investigate the galvanic coupling between two materials [24,46–48].
(2) Working electrode 2: The rod of low carbon steel of 2 mm in diameter was inserted in a square pure aluminum 20 mm × 20 mm then embedded in an epoxy resin. The surface area ratio Fe/Al is about 1/127.
(3) Working electrode 3: The low carbon steel was inserted in a pure aluminum rod as in (1) but in this case, the iron is spaced with the aluminum by 1 mm of epoxy resin, the whole electrode is embedded in an epoxy resin, the electric connection was made at the rear of the mounting. The surface area ratio Fe/Al is about 1/6.
(4) Working electrode 4: Two rods; low carbon steel and aluminum were embedded in an epoxy resin, the two electrodes were spaced by 1 mm and the electric connection was made at the rear of the mounting. The surface area ratio Fe/Al is 1/1.

The working electrode was polished with SiC paper up to the grade of 2400. An observation of the surface with an optical microscope was performed in order to check the surface state of the working electrode and the joined interface (working electrodes 1 and 2) after polishing. Electrolyte used for experiments was a 2.5 mM NaCl solution prepared with de-ionized water and sodium chloride at pH 5.40. This solution was used in a previous study [49]. The conductivity of this solution is sufficient ($k = 332\ \mu\text{S cm}^{-1}$) to allow corrosion processes, and sufficiently resistive to lead to measurable ohmic drops and then to provide a good signal to noise ratio with SVET. To this electrolyte, 2.5 mM of $CeCl_3 \cdot 7H_2O$ (supplied by Fluka Chemika, purity 98.5%) was added. In order to investigate the effects of the anionic part of cerium salts, electrolytes containing 10 mM NaCl + 2.5 mM of $Ce(NO_3)_3 \cdot 6H_2O$ (supplied by Aldrich, purity 99%) and 10 mM NaCl + 7.5 mM $NaNO_3$ (supplied by Merck extra pure) were used. The conductivity of different electrolytes is $1262\ \mu\text{S cm}^{-1}$, $1820\ \mu\text{S cm}^{-1}$ and $1818\ \mu\text{S cm}^{-1}$ respectively.

SEM and EDS analyses were carried out using a JEOL JSM 5900 LV high resolution scanning microscope equipped with an energy dispersive X-ray detector in order to investigate the mechanism of inhibition of cerium chloride.

The vibrating electrode used in this work was a commercial SVET manufactured by Uniscan, (Model 370). The microelectrode diameter is about 50 μm. The tip of the probe is platinized to increase the surface area open to solution and reduce the solution metal interface resistance. The microelectrode vibrated at a frequency of 80 Hz in perpendicular direction to the surface, with amplitude of 30 μm (peak to peak). SVET maps present local current density variations over an active (corroding) sample surface by measuring the voltage-drop variations close to the surface. The vibrating probe is used with a lock-in-amplifier to eliminate noise occurring at any frequency other than the frequency of probe vibration. The setup is equipped with one camera parallel to the sample surface in order to adjust the probe height. Scans were performed perpendicularly to sample surface. The probe height was adjusted to 180 μm. The choice of this working distance depends essentially on the magnitude of the current density on the electrode surface: the lower this current is, the lower must be the probe height [50,51]. Nevertheless, in the case of a galvanic coupling in free potential conditions, the probe height must be sufficiently low in order to detect an electric field. Moreover the probe height has to be adjusted not too low in order to limit any artifact resulting from conductivity gradient next to the electrode surface [51]. The setup used in this study allows to measure only the normal component of the current density. The microelectrode

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