Thermodynamic parameters of cerium(III) chloride heptahydrate precipitation on the surface of aluminium alloy 2024-T3 in chloride solution

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ABSTRACT:

In the present work the corrosion protection of aluminium alloy AA2024-T3 has been studied in chloride solution with and without addition of cerium(III) chloride heptahydrate ($CeCl_3$ x $7H_2O$). Inhibition efficiency as a function of concentration, temperature and exposure period of immersion (240 h) into 0.01 M NaCl, containing 3 mM, 4 mM and 5 mM of $CeCl_3$ x $7H_2O$, are investigated at 20 °C, 40 °C and 60 °C. Quantitative tests performed include electrochemical techniques, such as method of quasi-potentiostatic polarization (Tafel extrapolation) to determine corrosion current density (j_{corr}), inhibition efficiency (η), and degree of surface coverage (ϑ). The kinetic and thermodynamic parameters of adsorption process, such as activation energy (E_A), enthalpy of activation (ΔH_a^0), entropy of activation (ΔS_a^0), standard adsorption enthalpy (ΔH_{ads}^0), standard adsorption entropy (ΔS_{ads}^0) and the adsorption free energy (ΔG_{ads}^0) were also determined. Adsorption of the cerium ions on the AA2024-T3 surface follows the Langmuir isotherm model.

CONCLUSION:

The following conclusions can be drawn from these studies; Tafel plots indicates that the cerium (III) chloride heptahydrate can improve the corrosion resistance of aluminium alloy at temperatures of 20 °C, 40 °C and 60 °C. Immersion time, concentration and test solution temperature had an important influence on the corrosion properties due to many separate processes involved in precipitation that are each dependent on temperature. Immersion time (240h) before polarization, leads to formation of larger deposits on the S-phase, hindering the cathodic reduction of oxygen on Cu-rich intermetallics as well as anodic dissolution of Al and Mg from these intermetallics. The decrease of inhibition efficiency slightly with increasing temperature indicating that higher temperature dissolution of aluminium alloy predominates on adsorption of Ce^{3+} at the metal surface. Values of ΔG_{ads}^0, - 20 kJ mol^{-1} or lower, are consistent with the electrostatic interaction between the charged molecules and the charged metal surface (physical adsorption), while values less than - 40 kJ mol^{-1} mean the division or transfer of an electron from the molecule of the inhibitor to the metal surface in the process of forming a coordinate type of connection (chemisorption). Also, ΔG_{ads}^0 values increase with increasing temperature, additionally confirm that the inhibitor at higher temperatures show a lower tendency to the adsorption on the surface of AA2024-T3. Since the value of ΔG_{ads}^0 is between $-40 \leq \Delta G_{ads}^0 \leq -20$ 40 kJ mol^{-1} and value of ΔH_{ads}^0 is between - 20 < ΔH_{ads}^0 < 40 (endothermic process), adsorption of Ce^{3+} on the alloy surface is physisorption.

1. Introduction

Aluminium alloys containing copper (2000 series) exhibit high strength and are widely used in the aviation industry but generally they show low corrosion resistance and are susceptible to localized corrosion. The resistance of aluminium against corrosion in aqueous media can be attributed to a rapidly formed surface oxide film, which is composed of Al_2O_3, $Al(OH)_3$ and AlO(OH) phase. The potential difference between aluminum matrix and other intermetallic particle phases which give strength to these alloys would result in the occurrence of galvanic corrosion reaction in aggressive solution, especially with the presence of chloride ions (Cl^-), which shorten its service time significantly. The carcinogenic chromate pretreatments are currently used to hinder the localized corrosion of the AA2024-T3. However, stricter environmental regulations and the needs of industry stimulated an intense research effort to develop novel environmental-friendly pretreatments and inhibitors. Therefore, some rare earth salts are being employed to develop alternative environmentally friendly method to inhibit the corrosion protection of aluminium alloys.
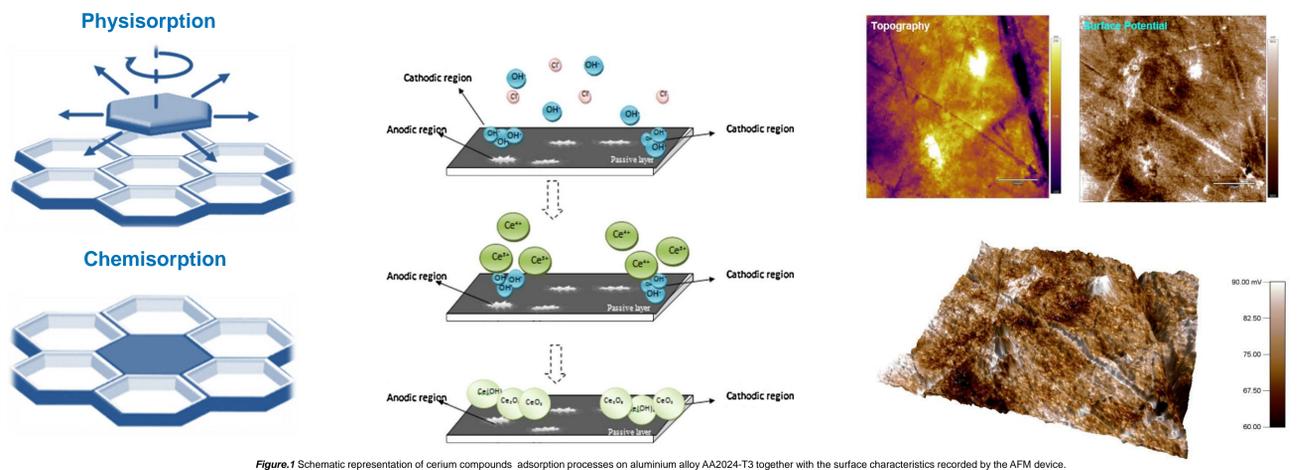
2. Physical and Chemical adsorption

Figure.1 Schematic representation of cerium compounds adsorption processes on aluminium alloy AA2024-T3 together with the surface characteristics recorded by the AFM device.

3. Experiment

The polished aluminium samples were immersed in 10 mM NaCl testing solution (50 mL) and into the NaCl solution doped with 3, 4 and 5mM concentrations of the $CeCl_3\cdot7H_2O$ for 240 h prior to the DC polarization tests. In order to investigate the corrosion behaviour of AA2024-T3, electrochemical measurements were performed in accordance with ASTM G5 and EN ISO 17475 standards, at three different temperatures (20 ± 2) °C, (40 ± 2) °C and (60 ± 2) °C. A three-electrode cell was used for Potentiodynamic Polarization measurements. The working electrodes used were cylindrical AA2024-T3 samples fixed in a glass rod. The counter and reference electrodes were graphite and (SCE) respectively.

4. Results & Discussion

In order to obtain more details on the corrosion process, a quantitative relationship between temperature and corrosion rate is given by Arrhenius's equation:

$$j_{corr} = A\exp\left(\frac{E_A}{RT}\right) \quad (1)$$

Obtained straight lines (see Fig. 2) have regression coefficient ($-E_A/R$) and section on the ordinate (lnA) from which E_A and A were calculated and then listed in Table 1.
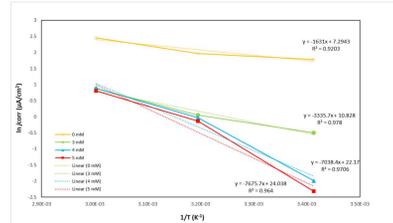

Figure.2 Arrhenius as a plots of ln j_{corr} versus 1/T in 0.01 mol/dm^3 NaCl at various concentrations of $CeCl_3$ x $7H_2O$ (0 mM, 3 mM, 4 mM and 5mM).

The magnitude of the activation energy may give an idea about the type of adsorption. Table 1 clearly shows that the activation energy values in the presence of inhibitors are higher than in uninhibited chloride solution (13,561 kJ / mol), which suggests that the energy barrier of the corrosion reaction increases with the concentration of $CeCl_3$ x $7H_2O$ inhibitors. The decrease of inhibition efficiencies with increasing temperature and the increase of E_A in the presence of the inhibitor, also indicate the physical adsorption mechanism.

Table.1 The parameters of Arrhenius's linear dependence (ln j_{corr} vs. 1/T) in 0.01 mol/dm^3 NaCl at various concentrations of $CeCl_3$ x $7H_2O$.

Concentration (mmol/dm³)	R²	E_A (kJ/mol)	A (μA/cm²)
0	0.92	13.561	1.471 x 10²
3	0.98	27.735	5.041 x 10³
4	0.97	58.521	4.249 x 10⁹
5	0.96	63.819	2.752 x 10¹⁰

Based on the results of polarization measurements at different temperatures and different concentrations of inhibitors, the two important kinetic parameters of corrosion were also calculated: enthalpy of activation (ΔH_a^0) and entropy of activation (ΔS_a^0) using the equation of transition state equation:

$$j_{corr} = \frac{RT}{Nh}\exp\left(\frac{\Delta S_a^0}{R}\right)\exp\left(-\frac{\Delta H_a^0}{RT}\right) \quad (2)$$

A plot of ln(j_{corr} /T) vs. 1/T (see Fig. 3) is the straight line with the slope ($-\Delta H_a^0/R$) and intercept [(ln (R/Nh)) + $\Delta S_a^0/R$)]. Kinetics parameters of the corrosion in NaCl solution in the absence and in the presence of inhibitor are presented in Table 2.
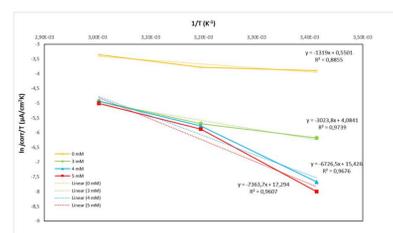

Figure.3 Arrhenius as a plots of ln j_{corr} /T versus 1/T in 0.01 mol/dm^3 NaCl at various concentrations of $CeCl_3$ x $7H_2O$ (0 mM, 3 mM, 4 mM and 5mM).

Table 2. Thermodynamic parameters of the corrosion in 10 mM NaCl as function $CeCl_3$ x $7H_2O$ concentrations.

Concentration (mmol/dm³)	R²	ΔH_a^0 (kJ/mol)	ΔS_a^0 (J/mol K)
0	0.89	10.967	-192.978
3	0.97	25.141	-163.595
4	0.97	55.927	-69.293
5	0.96	61.225	-53.761

The values enthalpy of activation ΔH_a^0 are positive in all systems (Table 2.) but they are higher in the presence of $CeCl_3$ x $7H_2O$ as well as they are continuously increasing with increased concentration of inhibitor. High negative values of the entropy of activation ΔS_a^0, both in the absence and in the presence of inhibitor ions, indicate formation of the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disorder takes place during the course of the transition from reactants to activated complex.

In order to get a better understanding of the electrochemical process on the metal surface, adsorption characteristics are also studied. Adsorption isotherms are very important in determining the mechanism of electrochemical reactions. The values of the adsorption free energy can be calculated using the equation:

$$\frac{\theta}{1-\theta} = K_{ads}C_{inh} \quad (3)$$

Figure 4 shows that the linear correlation coefficients (R^2) is almost equal 1, indicating that the experimental data fit well into the Langmuir adsorption isotherm.
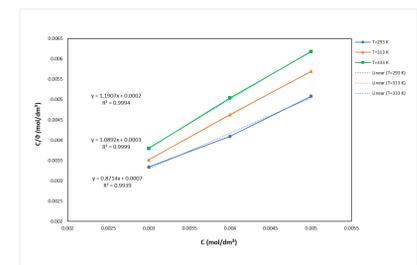

Figure.4 Curve fitting of the corrosion data for AA2024-T3 in 10 mM NaCl in the presence of different concentrations of $CeCl_3$ x $7H_2O$ to the Langmuir isotherm at different temperatures.

In addition, the equilibrium constant of the adsorption process increases with increasing temperature. Generally, large value of K_{ads} is bound up with a worse inhibition efficiency of a given inhibitor and its values are shown in Tables 3.

Table 3. Adsorption parameters of the linear regression between C/θ and C of $CeCl_3$ x $7H_2O$.

Temperature (K)	R²	K_{ads}	ΔH_{ads}^0 (kJ/mol)	ΔS_{ads}^0 (J/mol)	ΔG_{ads}^0 (kJ/mol)
293	0.9939	1428.57	25.563	181.06	-27.486
313	0.9999	3333.33	25.563	182.53	-31.568
333	0.9994	5000	25.563	180.99	-34.708

The values of ΔG_{ads}^0 and ΔH_{ads}^0 (see Table. 3) indicate the physical type of adsorption of Ce^{3+} compounds on the aluminium alloy surface.

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