



CERIUM-CYSTEINE COMPLEX INHIBITOR FOR ALUMINIUM ALLOY AA7075-T6

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Abstract: Aluminium AA7075 alloy with its low density and good mechanical properties, widely responds to the requirements of aerospace, navy, and defense industries. However, corrosion is the most common problem that affects the reliability and service life of components and constructions based on this alloy. One of the most practical methods for protecting metals from corrosion is the use of inhibitors. Chromates are known as excellent inhibitors but chromate compounds are highly toxic, carcinogenic, and thus hazardous to humans and the environment. The aim of this study was to synthesize an organic eco-friendly compound (cerium-cysteine) and to investigate its inhibitory property on aluminium alloy AA7075-T6. Rare-earth metals are effective and environmentally friendly substances for aluminium protection as well as cysteine that can be found in many proteins and enzymes such as the keratin in hair. The synthesized inhibitor was confirmed and analyzed by FTIR. The survey of samples corrosion resistance was conducted by three electrochemical methods: linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS), and polarization measurements (E_{pit}) in a 0.1M NaCl solution at room temperature. Different concentrations of cerium-cysteine were used to find the best efficiency. The best results were then tested for time dependence (up to 72 h). The inhibitory effectiveness of the cerium complex is shown to depend on a variety of factors such as concentration and time dependence.

Keywords: Cerium cysteine, corrosion inhibitor, NaCl solution, aluminium alloy AA7075-T6;

1. INTRODUCTION

Aluminium and its alloys are often used in the modern industry. Aluminium is considered to be the second metal that has a great engineering application. Due to its high strength, low density, thermal properties, and its ability to be highly polished, AA7075 aluminium alloy is widely used in manufacturing for the Military mostly for the Navy and Army.

7xxx series alloys such as AA7075 are often used in transport applications due to their high specific strength, including marine, automotive, and aviation [1].

The 7xxx series alloys provide improved protection at all their parts. This type of aluminium armor is extremely used in combat vehicles. Aluminium is extremely used:

- for improved vehicle mobility, "swimming ability", air transport, increased payload, and ease of maintenance.
 - for parts such as projectiles (both cartridge-launched and rocket), cartridges, mines, bombs, and their components
 - for making bridges and electronic hardware or other military equipment.
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The most important characteristic of aluminium is its corrosion resistance, its ability to form a protective film (i.e. Al_2O_3) on its surface. This corrosion resistance, however, deteriorates easily in acidic and basic media. The presence of chloride ions in the medium, especially in seawater or marine atmosphere conditions is unfavorable for aluminium and its alloys, because it produces pitting in an oxide film, thus reducing its corrosion resistance [1].

Appropriate means of protection must therefore be developed. The use of inhibitors in corrosion protection is the simplest, most economical, and efficient approach used in the industry. By adding inhibitors to the corrosive environment, the corrosion rate is reduced to an acceptable level.

So far, chromates have been used very successfully as excellent corrosion inhibitors. The mechanism of their action is based on the reduction of chromium from Cr^{6+} to Cr^{3+} ions and the formation of a protective film of chromium hydroxide on the metal surface. However, chromatic compounds are very toxic, carcinogenic, and dangerous to humans and the environment [2].

Nowadays, it is not enough for inhibitors to be only effective in protection against corrosion, but these compounds should be environmentally friendly with the least possible damage to human health. The aim of this paper is to examine an environmentally safe or green inhibitor that will show good protection of aluminium alloys (AA7075). Ecologically safe inhibitors can be divided into two categories: organic and inorganic eco-friendly/green inhibitors.

Among organic compounds, amino acids stand out as potential eco-friendly/green inhibitors. Amino acids are non-toxic, soluble in water, relatively inexpensive, biodegradable, and derived from nature [3, 4]. Cysteine is a very common

amino acid found in many proteins and enzymes, such as the keratin in hair, horn, and feathers. The chemical formula for cysteine is $\text{C}_3\text{H}_7\text{NO}_2\text{S}$ (Figure 1).

These acids contain two functional groups with different chemical nature: the amino ($-\text{NH}_2$) group with basic properties and the carboxyl group ($-\text{COOH}$). Sulfur-containing amino acids and a longer hydrocarbon chain showed a greater inhibitory effect. Additional groups, or groups that increase the electron density on the α -C atom, also have better inhibitory activity. Cysteine is an amino acid and contains of the amino group ($-\text{NH}_2$), a carboxyl group ($-\text{COOH}$), and a thiol group ($-\text{SH}$) and has the possibility of corrosion of various metals [5,6]. It can coordinate with the metal surface with all three groups, which gives it a large number of protection options.

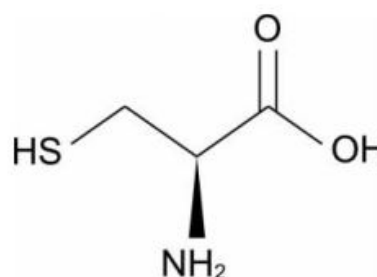


Figure 1. Chemical structure of the cysteine

Thus, the chemistry of L-cysteine is complex, it can represent different chemical forms depending on the pH of the solution. Different forms of L-cysteine depending on the pH of the medium are given in Figure 2.

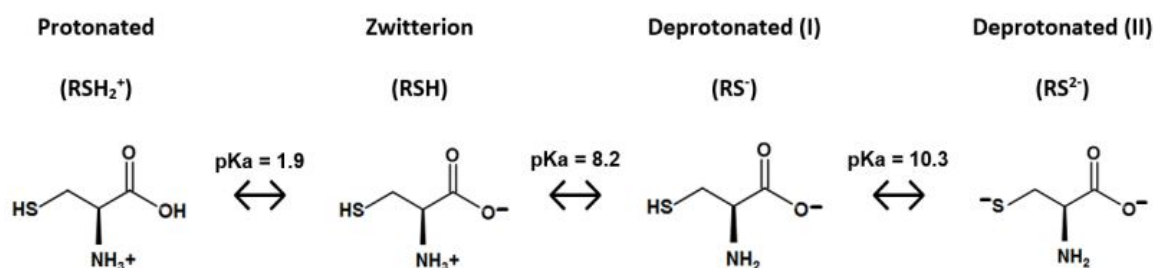


Figure 2. Forms of L-cysteine depending on the pH of the medium

Recently, in addition to organic, inorganic corrosion inhibitors have also been studied. The most famous are rare earth metals. Their salts have proven to be effective protection of aluminium alloys and are also not harmful to the environment. For now, it is known that cerium salts are very good corrosion inhibitors and cerium salts are more developed than other rare earths. [7, 8].

The aim of this study was to examine the inhibitory effect of the newly synthesized compound cerium-cysteine complex, by electrochemical methods.

3. EXPERIMENTAL

2.1. Materials

Metal sample AA7075-T6, supplied in a form of 30x50mm and 1,3mm thickness was used in this experiment. Its chemical composition is:

Zn	Mg	Cu	Fe	Cr	Si	other	Al
5.80	2.55	1.68	0.21	0.19	0.08	0.08	89.41

Before each measurement, samples were water-ground using SiC emery papers successively up to 1200 grit, rinsed thoroughly with deionized water, and cleaned in ethanol.

- The corrosive medium, 0.1 M NaCl, was prepared using sodium chloride, (99.0–100 % purity), supplied by Sigma Aldrich, and Milli-Q water with 18. MΩ cm resistivity at room temperature (25°C).
- The chemicals used for synthesis were cerium(III) chloride heptahydrate, CeCl₃·7H₂O (≥99.9% purity), and L-cysteine, C₃H₇NO₂S (97%) These chemicals were supplied by Sigma Aldrich or Fluka.

2.2. Synthesis of complexes

Synthesis of the cerium-cysteine complex was performed, in 1:3 ratio, as follows:

- 1 mmol CeCl₃ was placed into a reactor equipped with a stirrer, reflux condenser, and thermometer, and 15 mL of ethyl alcohol was poured. After dissolving, 3 mmol of L-cysteine was added; the reaction was carried out for 10 h at room temperature. After that, the reaction mixture was left to evaporate at room temperature and was dried in an oven at 40 °C. The obtained product were crystals with a yield of 60-70%. The synthesized compound was rinsed with methyl alcohol until it turned white. The product was dried again and ready for further researches.

2.3. Electrochemical measurements

Linear polarization resistance (LPR)

LPR measurements were carried out in a narrow range of potential, ±10 mV relative to corrosion potential E_{corr} , at a scan rate of 0.166 mV s⁻¹. The value of R_p was determined as the slope of the experimental $E-j$ curve, at the corrosion potential E_{corr} . Corrosion current density and corrosion rate were calculated using the experimental value of R_p . (Ref ASTM G 102).

Electrochemical impedance spectroscopy (EIS)

GAMRY Reference 1010E Potentiostat /Galvanostat/ZRA with a classic three-electrode cell arrangement was used to carry out the measurements. The working electrode was – AA7075, the counter electrode was - a Pt mesh, and the reference electrode - a saturated calomel electrode (SCE). Measurements were carried out at the corrosion potential (E_{corr}), over a frequency range from 100 000 Hz to 0.1 Hz using a 10 mV amplitude of the sinusoidal voltage. The experimental EIS results were fitted with the Gamry Elchem Analyst fitting procedure.

Linear Sweep Voltammetry (LSV)

The LSV technique is used to obtain cathode and anode polarization curves. The metal, which is in a corrosive environment, is polarized in the potential range $E = \pm 0.250$ V in relation to E_{corr} , with the registration of the corresponding current i . From the obtained graph $E - \log i$, the corrosion current density i_{corr} can be obtained directly,

by extrapolating the linear part of the anode and / or cathode polarization curve to the corrosion potential E_{corr} .

The %IE was calculated from the measured i_{corr} values using the following equation:

$$\%IE = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}} \times 100 \quad (1)$$

where i_{corr}^0 and i_{corr} are the corrosion current density in the absence and presence of inhibitor.

The solution of the cerium-cysteine complex was made by dissolving crystals in deionized water at a concentration of 300 ppm. Electrochemical measurements were carried out without inhibitor and with inhibitor in 0.1M NaCl (pH = 5.6) solution. In a cell with 130 ml of NaCl solution different portions of inhibitor were added in order to identify the most efficient one. Then, the optimal concentration of the inhibitor was chosen and tested in the function of time for 3 days.

3. RESULTS AND DISCUSSION

3.1. Polarization measurements

The inhibitor was added to a volume of 20 ml, however, the inhibitory properties were shown to be optimal at 10 ml. The results obtained by the LPR method showed that the growth trend of the inhibitory effect, i.e. the protection of metals from corrosion, reached a constant line and there was no need to continue measuring further. **Table 1** shows the corrosion parameters and inhibitor efficacy

Table 1. Corrosion parameters, obtained by the LPR method, for AA7075 in 0.1 M NaCl without and with different amount of inhibitor cerium-cysteine

Complex cerium-cysteine (300 ppm)	LPR			
	MI	E_{corr} (mV)	R_p (Ω cm ²)	E (%)
0		-708	7 644	/
0,5		-705	13 200	42.1
1		-701	14 720	48
2		-702	16 310	53.3
3		-702	20 470	62.7
4		-701	20 780	63.2
5		-700	25 430	69.9
7		-702	28 650	73.3
10		-696	37 300	79.5

According to the results inhibitor can be classified as an anodic- or cathodic-type inhibitor when the change in E_{corr} is greater than 85 mV. From **Table 1** it can be seen that this complex looks like a mixed-type inhibitor, which is characteristic of cysteine. In order to obtain additional information on electrochemical phenomena that take place on the metal-solution surface, without the presence and with the presence of inhibitors, EIS impedance measurements were performed.

3.2. EIS measurements

The function of the inhibitory effect depending on the change in concentration is given in the Nyquist diagram of **Figures 3**. (where **3a** represents the overall picture, while **3b** represents an enlarged graph to see the differences in the slope of the curve).

After the optimal concentration was determined, the inhibitor was tested for time dependence. The Nyquist diagram of **Figure 4** shows how the inhibitor behaves for 3 days, and also provides information on how the 0.1 M NaCl solution behaves without the inhibitor. The values are given in **Table 2**.

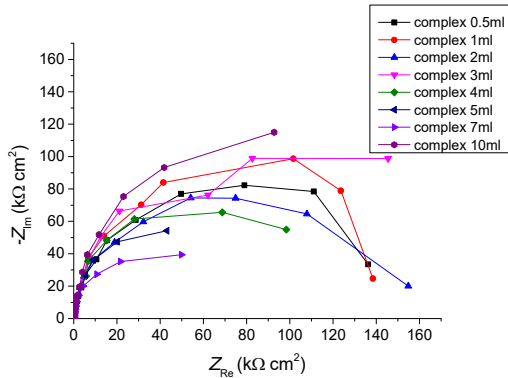


Figure 3a. Nyquist plot for AA7075 in 0.1 M NaCl (pH=5.6) without and with different concentrations of inhibitor cerium-cysteine complex

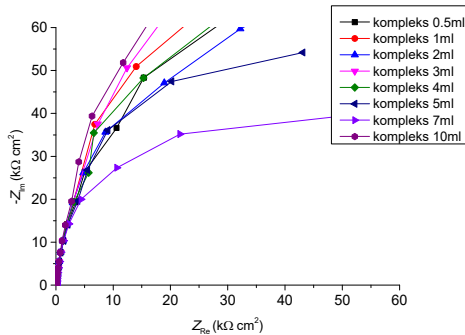


Figure 3b. Nyquist plot for AA7075 in 0.1 M NaCl (pH=5.6) without and with different concentrations of inhibitor cerium-cysteine complex

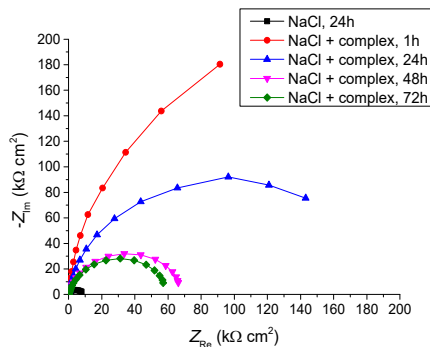


Figure 4. Nyquist plot for time dependence of AA7075 (pH = 5.6) dissolution in the presence of inhibitor cerium-cysteine complex at optimum concentration (0.045 mM)

Table 2 Corrosion parameters versus time, obtained by the EIS methods, for AA7075 in 0.1 M NaCl (pH=5.6) without and with cerium-cysteine complex

EIS			
t, h	E_{corr} (mV)	R_p ($\Omega \text{ cm}^2$)	IE (%)
0.1M NaCl	-721	8 238	/
0,5h	-728	550 500	98.41
24h	-831	203 500	95.95
48 h	-804	71 840	88.53
72h	-804	63 300	86.99

3.3. LSV measurements

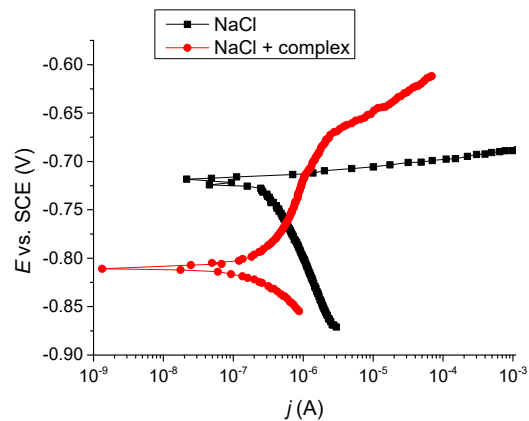


Figure 5. Potentiodynamic polarization plot for AA7075 in 0.1 M NaCl in the absence and presence of an optimum concentration of cerium-cysteine at 25°C.

Various electrochemical phenomena, including electrochemical polarization and passivation, can be explained by the potentiodynamic polarization method.

Figure 5 shows the anodic and cathodic polarization curves with and without the presence of inhibitors in 0.1M NaCl. The corrosion current density is calculated by extrapolating the cathode and anode linear segments of the Tafel curve.

Table 3 presents the values of different potentiodynamic parameters: corrosion current density (i_{corr}), corrosion potential (E_{corr}), and pitting corrosion resistance ($E_{pit} - E_{corr}$).

The results show that the i_{corr} value decreased in the presence of the inhibitor, indicating that the inhibitor adsorbed to the metal surface in 0.1M NaCl.

In this work, the maximum shift of the E_{corr} value was 95 mV, suggesting that it is a cathodic type of inhibitor. From **Table 3** it can be noticed that the inhibitor has a pronounced inhibitory effect and affects the cathodic rather than the anodic reaction, which is characteristic of cerium. Also, in the presence of inhibitors, the metal has resistance to pitting corrosion, while without the presence of inhibitors this is not the case.

Table 3. Tafel polarization parameters (\pm SD) for AA7075 in 0.1 M NaCl solution in absence and presence of optimum concentration of cerium-cysteine complex.

Inhibitor	E_{corr} , mV	i_{corr} , μA	E_{pit} , mV	$E_{\text{pit}}-E_{\text{corr}}$
0.1M NaCl	-715	0.35	-705	15
Complex	-810	0.12	-675	135

3.4. Adsorption isotherm

The adsorption isotherm can be determined by assuming that the inhibitory effect is mainly due to adsorption at the metal-solution interface. Basic information on the adsorption of inhibitors on a metal surface can be obtained by using the adsorption isotherm. The Langmuir isotherm is given by the following equation:

$$\frac{\theta}{1-\theta} = K_{\text{ads}}C \quad (2)$$

where K is the equilibrium constant of the adsorption process and C is the molar concentration of the inhibitor. The plot of c/θ versus C gave a straight line as shown in **Figure 6**. The linear regression coefficients (R^2) are almost equal to 1, confirming that the adsorption of the studied inhibitor in 0.1 M NaCl solution follows the Langmuir's adsorption isotherm.

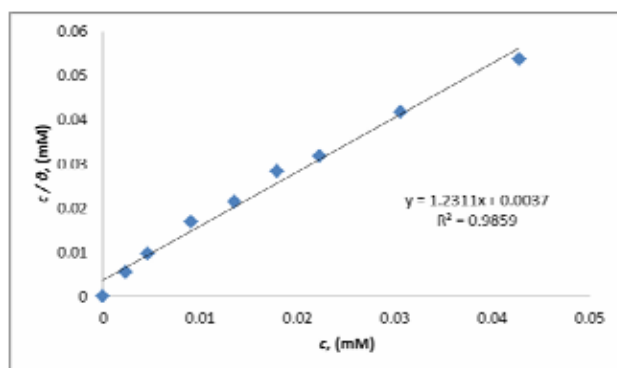


Figure 6. Langmuir's isotherm for adsorption for AA7075 in 0.1M NaCl in the presence of inhibitor cerium-cysteine complex

The free energy of adsorption (dG_{ads}) is related to the adsorption constant (K) with the following equation:

$$K_{\text{ads}} = \frac{1}{55.5} \exp\left(\frac{\Delta G^{\circ}}{RT}\right) \quad (3)$$

In this case, a kinetic model could be used to explain the dissolution process of aluminium alloy in the NaCl solution because the linear regression coefficients are close to 1.

The calculated values for K_{ads} and G_{ads} for the cerium-cysteine complex are given in **Table 4**.

Table 4. Thermodynamic parameters for 0.1 M NaCl solution without and with the inhibitor cerium-cysteine for different concentration, on AA 7075.

T=25 °C (298 K)		
cerium-cysteine c, mM	K_{ads}	ΔG_{ads} , KJ/mol
0	0	0
0.0023	1.83817349	-11.4591556
0.0046	1.04851111	-10.0682436
0.0090	0.59539568	-8.66618497
0.0135	0.46737488	-8.0663784
0.0179	0.35531824	-7.38723167
0.0222	0.31708126	-7.10514588
0.0306	0.2413113	-6.42859453
0.0450	0.18723619	-5.79999262

Generally, a higher value of K_{ads} is associated with strong adsorption and higher inhibition. K_{ads} follows ΔG_{ads} , which means that K_{ads} values decline with the increase of Gibbs energy. In **Table 4**, this trend is accompanied by an increase in concentration. The negative ΔG_{ads} values ensure spontaneous adsorption and lead to a stable adsorbed layer on the aluminium alloy surface. A value of ΔG_{ads} -20 kJ mol or lower shows electrostatic interaction between charged organic molecules presented in bulk solution and charged metal surface.

On the other hand, a ΔG_{ads} at a value near or greater than -40 kJ mol involves charge sharing or transferring between the organic molecules and the metal surface. The results for the synthesized organic inhibitor (cerium-cysteine complex) show that ΔG_{ads} is more positive with increasing concentration. The ΔG_{ads} values indicate physical adsorption (**Table 4**).

5. CONCLUSION

From the obtained results the following can be concluded:

1. Cerium-cysteine complex acts as a good corrosion inhibitor for AA7075 in 0.1 M NaCl solution. Inhibition efficacy increases with increasing inhibitor concentration.
2. The cerium-cysteine complex is a mixed type of inhibitor. Namely, in the first period (~ 5 h) cysteine acts as a mixed inhibitor, and after cerium takes the role of protection and acts as a cathodic inhibitor.
3. The data obtained by electrochemical measurement and kinetic calculation show that adsorption takes place mainly by physisorption.
4. Adsorption of the test inhibitor follows the Langmuir isotherm well.

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References

- [1] T Hashimoto, S Jyogan (Showa Aluminium), K Nakata, Y G Kin And M Ushio (Osaka University): Fsw Joining Of High Strength Al Alloy
- [2] Kendig MW, Buchheit RG. Corrosion inhibition of aluminium and aluminium alloys by soluble chromates, chromate coatings and chromate-free coatings. *Corrosion*. 2003;59:379–400
- [3] J.J. Fu, S.N. Li, L.H. Cao, Y. Wang, L.H. Yan, L.D. Lu, Computational and electrochemical studies of some amino acid compounds as corrosion inhibitors for mild steel in hydrochloric acid solution, *J. Mater. Sci.* 45 (2010) 979
- [4] H. Saifi, M.C. Bernard, S. Joiret, K. Rahmouni, H. Takenouti, B. Talhi, Corrosion inhibitive action of cysteine on Cu–30Ni alloy in aerated 0.5 M H₂SO₄, *Mater. Chem. Phys.* 120 (2010) 661
- [5] M.A. Amin, K.F. Khaled, Q. Mohsin, H.A. Arida, A study of the inhibition of iron corrosion in HCl solution by some amino acids, *Corros. Sci.* 52 (2010) 1684.
- [6] H. Cang, Z. Fei, W. Shi, Qi Xu, Experimental theoretical study for corrosion inhibition of mild steel by L-cysteine, *Int. J. Electrochem. Sci.* Y 10121 (2012).
- [7] D. Zhao, J. Sun, L. Zhang, Y. Tan, J. Li, *J. Rare Earths* 28 (2010) 371–374.
- [8] M. Forsyth, T. Markley, D. Ho, G.B. Deacon, P. Junk, B. Hinton, A.E. Hughes, *Corros. Sci.* 64 (2008) 191–197.