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Electrochemical synthesis of polyaniline coating on Pb alloy for high corrosion protection performance

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Abstract

Polyaniline (PANI) coating was electropolymerized on Pb alloy surface using cyclic voltammetry technique in a sulfuric acid solution containing aniline monomers. The corrosion performance of PANI coatings in 1M H₂SO₄ solutions was investigated by an electrochemical method such as potentiodynamic polarization technique. The influence of parameters such as cycle number, aniline concentration as well as scan rate on the anticorrosion properties of PANI film was investigated. The polyaniline coating exhibited a strong decrease of corrosion current in the acidic medium compared to the bare substrate and corrosion potential increased from -0.543 V vs SCE for uncoated alloy to 0.425 V for polyaniline coated lead alloy electrode. The results indicated that Polyaniline coating effectively protected Pb alloy from corrosion in acidic solutions, suggesting its potential as a coating material for corrosion protection of lead alloy in aqueous corrosive environments.

Keywords:

Pb alloys, Polyaniline, Electrochemical polymerization, Cyclic voltammetry, Corrosion protection.

1. Introduction

Lead and its alloys are regarded as essential metals due to their extensive use

in a variety of industrial applications, including electroplating containers, electrosynthesis electrodes, wastewater

electrochemical treatment, electrowinning anode materials, and lead–acid battery grids and plates [1]. In such applications, the life of lead and lead alloys may be limited as a result of corrosion or the formation of an insulating passive layer of lead-based materials on their surface [2].

Metals can be safeguarded from corrosion through the utilization of protective coatings (or linings), inhibitors, and cathodic or anodic protection strategies [3]. Recently, numerous studies have focused on the usage of conducting polymers as sophisticated coating materials across various fields, owing to their environmentally friendly characteristics, straightforward synthesis process, excellent stability, and redox properties, which make them promising for the corrosion protection of metals [4, 5]. The development of a shielding layer to prevent the assault of corrosive agents, which is referred to as the barrier effect, explains the protective properties of the CP coating [6, 7]. Conversely, CPs can be considered as a protective anode due to the presence of a CP film in its oxidized state, providing the metal passive with a high open circuit potential [6].

Polyaniline (PANI) is one of the most promising conducting polymers owing to its high conductivity, environmental stability and lack of

toxicity, simplicity of synthesis, and low cost [8-10]. The protective properties of PANI may result from the passivation of metal in extremely acidic environments [5, 9]. PANI has demonstrated a capacity to protect against corrosion by catalyzing the formation of a passivating oxide layer [5].

The electrochemical synthesis (ES) of polyaniline is frequently performed on noble metal, carbon glass, and $\text{In}_2\text{O}_3/\text{SnO}_2$ electrodes. The ES of PANI on non-noble metal electrodes is the topic of just a few studies [11]. This process is complicated because It is important to acknowledge that the primary issue encountered during the electrodeposition of PANI on lead and other active metals was the poor adhesion of the electrodeposited polymer to the metal surfaces and the increased rate of metal dissolution in corrosive media, Which led to a more difficult deposition [12-14]. Nevertheless, this problem could be handled by depositing a passive layer at the electrode, either before or during the polymer deposition process. [15, 16]. To get started with electropolymerization, a rather high anodic potential must be provided, and an appropriate acid must be used for passivation. [11, 17, 18].

Thus, in this work, we attempt to synthesize adherent polyaniline coating on lead alloy substrate by cyclic voltammetry method from aqueous H_2SO_4

solution and examine its ability to serve as corrosion protective coating on lead alloy. To the best of our knowledge, there are no reports in the literature dealing with the direct deposition of polyaniline coating on lead alloy from aqueous solution. The objectives of the present study are: (a) to find appropriate conditions, low-cost, and easily available electrolyte for the electrochemical synthesis of polyaniline coating on lead alloy substrate (b) to examine the possibility of utilizing the polyaniline coating for corrosion protection of lead alloy in aqueous 1M H₂SO₄ solution; (d) to assess synergistic effects of PANI on the anticorrosion performance of the underlying Pb alloy.

2. Experimental

2.1. Materials

Aniline (C₆H₇N) and sulfuric acid (98% H₂SO₄) were purchased from Sigma Aldrich chemical industries. Aniline was freshly distilled and stored in the dark. All chemicals were reagent grade and were used as received without any further purification. Solutions involved were prepared with distilled water. For each run, freshly prepared solutions were used.

2.2. Electrochemical instruments

Electrochemical experiments were carried out with a three-electrode one-

compartment glass cell. We used a saturated calomel electrode (SCE) as the reference electrode, a Pt rod as the counter electrode, and a lead alloy rod electrode with a 7 mm diameter (7 cm × 4.5 cm dimension made by die casting method) as the working electrode.

The rod form of Pb alloy electrode was insulated with polyester resin and thus only its cross-section (1 cm²) was allowed to contact the electrolyte. The main chemical composition of Pb alloy is (wt%): 0.001% of Ca, 0.2% of Sn, 1.4% of Sb and remaining Pb. Before experiments, Pb alloy surface was polished using grit emery papers (320 - 1000 grade), washed with distilled water, and then degreased with acetone or ethanol.

All electrochemical measurements were carried out at room temperature. Electrochemical experiments were performed using a potentiostat (BioLogic SP-50/150, Model VMP3 -Version 10.38).

2.3. Electrodeposition of polyaniline (PANI) coating

Electropolymerization was carried out by cyclic voltammetry (CV) in aqueous solutions containing different concentrations of aniline (ANI) between 0.05 to 0.4 M in 1 M sulfuric acid as a supporting electrolyte in the potential range from 1.15 to 1.85V vs SCE using

different scan rates (between 10 to 25 mV/sec), as well different number of cycles (from 10 to 40 cycles). After polymerization the coated lead alloy was rinsed with deionized water and used directly for electrochemical measurements.

2.4. Electrochemical measurements

Electrochemical corrosion tests were carried out to investigate the corrosion performance of PANI film on the lead alloy using potentiodynamic polarization technique (PDP). The study of optimum conditions was investigated to obtain the best protection efficiency of PANI coatings. The working electrode was first immersed in the test solution for 30 min to establish a steady state open circuit potential (OCP). Potentiodynamic polarization measurements were measured at ± 100 mV versus OCP at the scan rate of 5 mV/s. From the anodic and cathodic polarization curves, the Tafel regions were identified and extrapolated to the corrosion potential (E_{corr}) to obtain the corrosion current (I_{corr}) using EC-Lab software. Electrochemical corrosion measurements were performed in a highly corrosive solution of 1 M H_2SO_4 at room temperature and in open air.

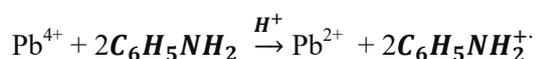
3. Results and discussions

3.1. Electrosynthesis of PANI on lead alloy electrode

Cyclic voltammetry (CV) is an effective method for the electrodeposition of organic conductive polymers, particularly polyaniline, onto oxidizable electrode surfaces [19]. Although numerous electrochemical techniques are appropriate for the nucleation and growth of PANI on inert electrodes, cyclic voltammetry generates homogenous and dense PANI layers [20]. From electrochemical studies of Pb alloy in sulfuric acid [21-24], The quality of the electropolymerization of PANI on the Pb alloy surface is dependent upon the nature of the passive layer that is formed prior to the electrodeposition of PANI. The poor conductivity of PbO and PbSO_4 layers prevents the electropolymerization of PANI. However, the dissolution rate of PbO_2 layer is reduced without preventing electropolymerization.

Fig. 1 shows the CVs obtained during the electropolymerization of aniline in 1 M H_2SO_4 solution at different cycle numbers in the potential range from 1.15 to 1.85 V (vs. SCE) at a scan rate of 10 mVs⁻¹. In the first to third cycles, the electrode was covered with PbSO_4 , so no apparent oxidation peak is observed, therefore it is fully insulating.

Consequently, the electrode's conductivity increased, and the rate of PbO_2 formation increased after the third cycle due to PbO_2 formation. However, in addition to the electrochemical oxidation of aniline, PbO_2 also underwent chemical oxidation at this potential. Further, PbO_2 reacts with aniline to produce an anilinium cation radical that can initiate a polymerization reaction. This reaction corresponds to the following reaction:



During the successive recording of cyclic voltammograms, the potential of

the oxidation peak and reduction shift significantly to more positive and negative values, respectively. The current intensities of oxidation and reduction peaks increase uniformly in response to the displacement of this potential, demonstrating that the Pb alloy surface underwent a continuous deposition of PANI and that the resulting PANI was both electrochemically active and conductive. After several cycles, the current intensity and the potential of the various peaks settled down, indicating that the coatings attained thermodynamic and kinetic stability on the electrode.

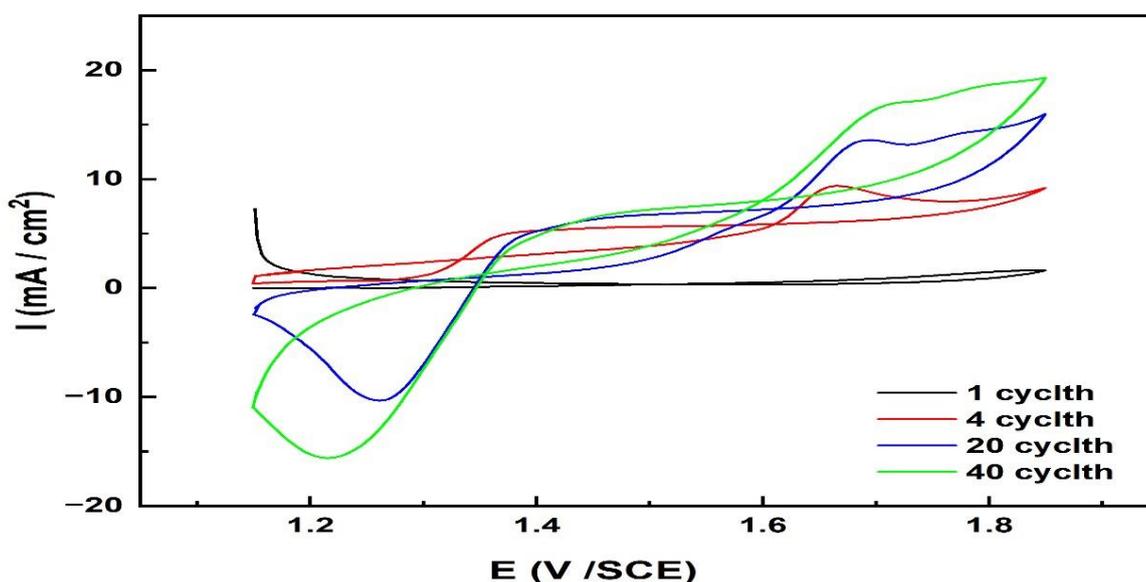


Fig. 1: CVs during the electropolymerization of aniline in 1 M H_2SO_4 solution on the Pb alloy substrate in the potential range from 1.2 to 1.8V (vs. SCE) at a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$. Scans 1, 4, 20 and 40 are displayed.

3.2. Corrosion tests

3.2.1. Potentiodynamic polarization studies (PDP)

The inhibition performances of the pure polyaniline and its composite coatings on lead alloy prepared under various conditions were analyzed in 1 M H₂SO₄ solution using potentiodynamic techniques. These profiles yielded the electrochemical parameters: corrosion potential (E_{corr}), corrosion current density (I_{corr}), and anodic and cathodic Tafel slopes (β_a and β_c). The following equation was employed to estimate the corrosion inhibition efficiency (η) of the coating [25]:

$$\eta = \frac{I_{\text{Pb}} - I_{\text{coat}}}{I_{\text{Pb}}} \times 100\%$$

where, I_{Pb} and I_{coat} were the corrosion current density of the Pb alloy samples without and with coatings, respectively.

3.2.1.1. Effect of the cycle number

Figure 2 shows the potentiodynamic polarization (PDP) curves recorded in 1 M H₂SO₄ medium for an uncoated Pb alloy and polyaniline-coated Pb alloy. Corrosion current density (I_{corr}), corrosion potential (E_{corr}), anodic slopes, cathodic slopes, and corrosion inhibition efficiency were obtained from the polarization curves and presented in Table 1.

Table 1. Electrochemical polarization parameters for uncoated and polyaniline-coated Pb at various cycle numbers in 1 M H₂SO₄ solution.

Cycle number	E_{corr} (V)	I_{corr} (μA)	β_a (mV/dec)	β_c (mV/dec)	CR (mm/year)	%IE
Blank	-0.543	630.77	55.2	79.9	9.419	---
10	0.361	167.45	121.4	79.8	2.501	73.45
20	0.377	78.77	133.8	94.8	1.176	87.51
30	0.419	39.84	128.1	97.1	0.595	93.68
40	0.425	22.12	123.4	93.1	0.332	96.49

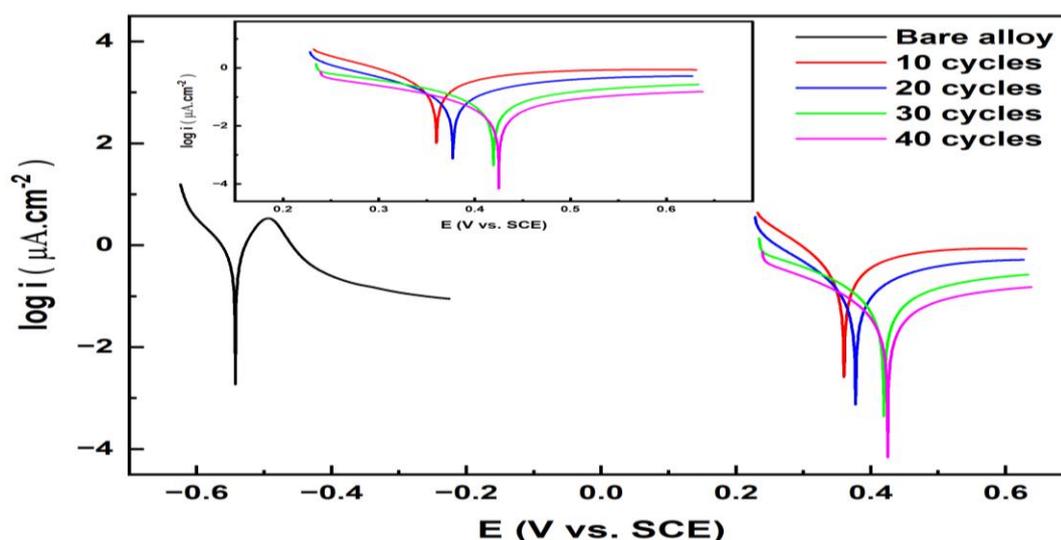


Figure 2. The potentiodynamic polarization curves for uncoated and polyaniline coated Pb alloy in an aqueous solution containing 1M H₂SO₄ and 0.1M ANI at 10mV/s at various cycle numbers.

The coated sample displayed lower values than the bare sample, and its corrosion potential shifted in the anodic direction. This result highlighted the protective properties of the coating against a corrosive environment. The plots exhibited a decrease in corrosion current density (I_{corr}) and a slight increase in corrosion potential (E_{corr}) towards more positive values for the coated surface as the number of cycles increased, suggesting an enhancement in inhibition efficiency. The improvement in inhibition efficiency with a greater number of cycles implies that the stability of the coated polymer layer on the lead alloy surface improves as the cycles increase, hence enhancing inhibition efficiency.

3.2.1.2. Effect of ANI concentration

The composition of the coating was adjusted by aniline concentrations in the electrolyte solutions. The coating was prepared at different aniline concentrations (0.05-0.4 M) with a fixed deposition potential window (1.15 – 1.18V) and cycling number (40 cycles).

As shown by the Tafel polarization curves (in Fig. 3 and Table 2), I_{corr} decreased from 67.56×10^{-6} to 22.12×10^{-6} A cm⁻² as aniline concentrations increased from 0.05M to 0.1M. However, as aniline concentrations further increased, the corrosion rate of coating became worse with the decrease of corrosion inhibition efficiency from 96.49% to 93.59% which means that polymer degradation may be occurring.

3.2.1.3. Effect of scan rate

The corrosion protection performance of the polyaniline coatings synthesized after 40 cycles at different scan rates was examined in an aqueous 1M H₂SO₄ solution using PDP studies depicted in Figure 4. The tabulated data (Table 3) shows that i_{corr} values increase

significantly as the applied scan rate of electropolymerization reaction increases and this is attributed to the decrease in the film thickness. Such behavior points out that the most effective protection against corrosion of Pb alloy was reached when the scan rate was 10 mV/s.

Table 2. Electrochemical polarization parameters for uncoated and polyaniline coated Pb at various aniline concentrations in 1 M H₂SO₄ solution.

ANI CONC. (M)	E_{corr} (V)	I_{corr} (μA)	β_a (mV/dec)	β_c (mV/dec)	CR (mm/year)	%IE
Blank	-0.543	630.77	55.2	79.9	9.419	---
0.05	0.346	67.56	120.5	83.9	1.009	89.29
0.10	0.425	22.12	123.4	93.1	0.332	96.49
0.20	0.368	40.38	114.4	86.0	0.603	93.59
0.30	0.392	44.87	101.2	90.9	0.670	92.89
0.40	0.351	57.41	167.0	109.5	0.857	90.89

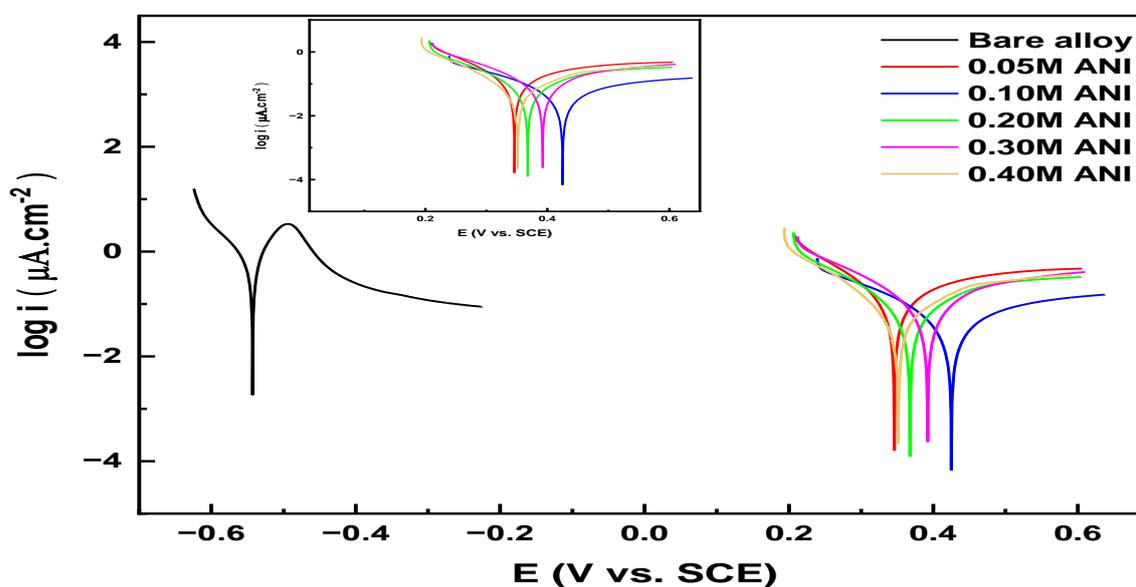


Figure 3. The potentiodynamic polarization curves for uncoated and polyaniline-coated Pb alloy at different aniline concentrations in 1 M H₂SO₄ solution.

Table 3. Electrochemical polarization parameters for polyaniline-coated Pb at various scan rates in 1 M H₂SO₄ solution.

Scan rate (mV/s)	E _{corr} (V)	I _{corr} (A)	β _a (mV/dec)	β _c (mV/dec)	CR (mm/year)	%IE
10	0.425	22.12	123.4	93.1	0.332	96.49
15	0.403	36.53	118.6	94.4	0.546	94.21
20	0.389	56.42	120.2	93.6	0.843	91.06
25	0.347	69.23	163.5	99.4	1.023	89.02

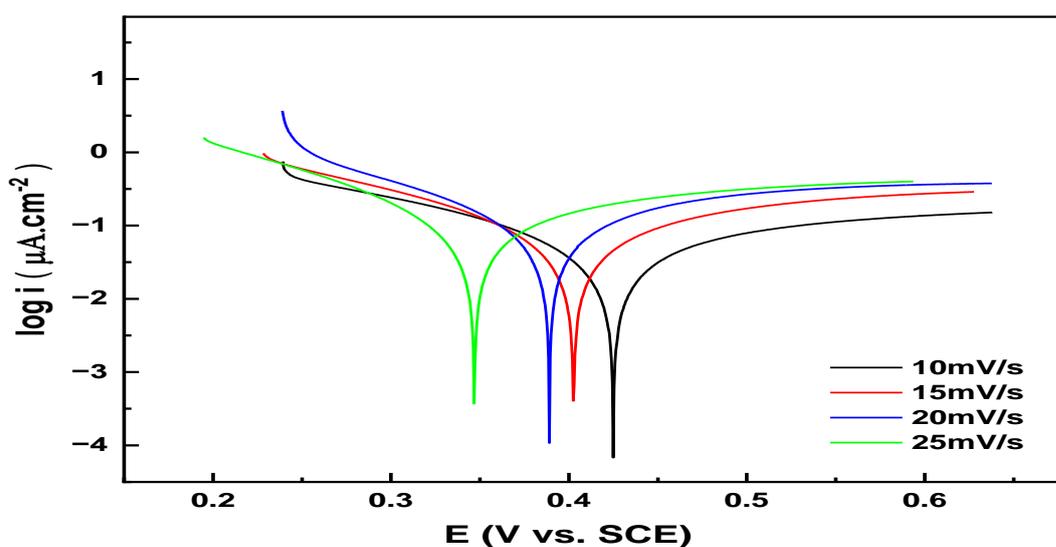


Figure 4. The potentiodynamic polarization curves for polyaniline-coated layer on Pb alloy at different scan rates in 1 M H₂SO₄ solution.

3.3. Mechanism of corrosion protection

The anodic protection mechanism is commonly employed to explain the protection of metals utilizing polyaniline-based coatings. The polyaniline-metal interface is modified to form passivating layers, facilitating charge transfer reactions between the metal and PANI.

The anodic protection mechanism is characterized by the shift of corrosion

potential into the passive area for the selected metal and corrosion environment. To achieve passivation, the corrosion potential must be anodically moved (ennobled) into the passive zone. The value of the passivation potential is contingent upon various parameters, including the composition and nature of the corrosive medium, as well as the type of coated metal or alloy [19].

Figure 5 shows the schematic mechanism of electropolymerization process of aniline in sulphuric acid. As shown in Figure 5, primarily SO_4^{2-} rather than HSO_4^- interacts with the polymer when exposed to sulfuric acid to produce a bidentate system, as assumed by Lippe

and Holze [26]. The findings acquired from the analysis of polymer film stated that PANI coatings provide superior protection to the Pb alloy surface against nucleophilic assault by SO_4^{2-} ions, which stimulates the substrate's dissolution process.

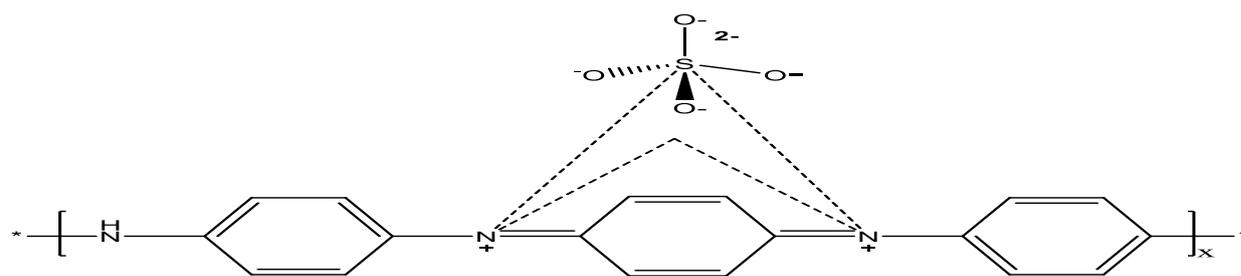


Figure 5. Schematic mechanism of electropolymerization process of aniline in sulphuric acid.

4. Conclusion

- Electrochemical polymerization of aniline on Pb alloy substrate was successfully performed with the high quality of deposition accomplished in sulphuric acid.
- The right choice of synthesis parameters for conjugated polymers (CPs) can enhance the anticorrosion behavior of the coatings for metals and their alloys.
- Polyaniline coating provides protection against corrosion of Pb alloy in acidic solutions, and it can be considered as a potential coating material for corrosion protection of lead alloy in aqueous corrosive solutions.

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