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Corrosion Inhibition of Laser Welded Mg AZ31B-H24 Alloy in NaCl Medium Using Pectin as an Eco-Friendly Inhibitor

V. Balaji[1,2], V.K. Bupesh Raja[1*], Jagadeesan Saranya[2]

[1] *School of Mechanical Engineering, Sathyabama Institute of Science and Technology, Chennai, 600119, INDIA*
[2] *Department of Humanities and Sciences, Gokaraju Rangaraju Institute of Engineering and Technology, Hyderabad, 500090, INDIA*

*Corresponding Author: bupesh.v.k@gmail.com
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Abstract

A magnesium alloy material possesses properties like stiffness, strength, chemical activity, good machinability, etc. which loses its corrosion resistance caused by the chemical activity of active magnesium. To control the corrosion of magnesium AZ31B-H24 alloy, an eco-friendly, water-soluble, cheap, and readily available inhibitor like pectin can be used as an inhibitor in a 5% NaCl medium. To confirm the adsorption of inhibitor molecules on the metal surface, weight loss and surface studies (SEM) were carried out. In addition, the Langmuir adsorption isotherm also confirms the presence of a monolayer on the magnesium surface. The results revealed that the pectin molecules acted as an efficient inhibitor for both welded and non-welded specimens of Mg alloy.

1. Introduction

Magnesium-based-AZ31 B H24 and its alloys have been recognized as a promising material to substitute heavy metal alloys shortly and it is extensively used in the fields of automobiles, military, energy storage, aerospace, etc. due to its good machinability, strength, electromagnetic properties, etc. [1]. However, this material is prone to corrosion which would be a barrier to the aforementioned applications.

Various preventive methods have been developed to control magnesium corrosion.; the addition of inhibitors is the classical method to control the corrosion process of Mg [2]. This method is economically safe, easy to operate, and does not require special equipment. Types of inhibitors include ionic liquids, organic, polymers, bio waste, natural products, etc. These inhibitors play a major role in preventing corrosion. In this study, a natural water-soluble polymer is chosen to prevent the Mg alloy AZ31B-H24 on welded and non-welded in 5% NaCl. Organic and ionic liquid inhibitors require more time to synthesize, which are toxic, costly, and not safe for the environment whereas the natural water-soluble polymers are safe, cheap, eco-friendly, etc. Pectin also contains oxygen, hydroxyl group, and π bonds in its structure which are favorable for adsorption and thus prevent the metal from corrosion [3-5]. In this work, the corrosion protection of welded and non-welded specimens of Mg alloy AZ31B-H24 is investigated by weight loss and SEM (Scanning Electron Microscopy) techniques.

2. Materials and Methods

AZ31B-H24 magnesium alloy based on Mg has Al (2-3), Zn (0.5-1.2), Mn (0.19), Si (0.09), Fe (0.003) and Cu (0.02) (wt.%). Before weight loss and surface studies, the specimens (20 x 10 x 5 mm) were polished using abrasive papers with 200, 400, 800, and 1200 grades to remove surface oxides. After polishing, the specimens were rinsed with distilled water, and crystalline compound-based ethanol was used for cleaning purposes [6]. The cleaned electrodes are finally dried in the air. The chemical structure of a commercial pectin inhibitor is shown in Fig. 1. Pectin was dissolved in a 5% NaCl solution and prepared for weight loss (WL) testing and surface analysis.

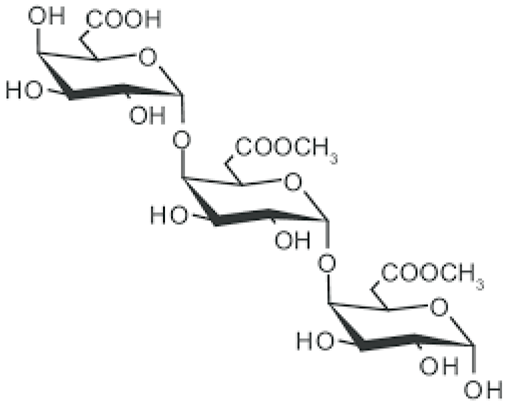

Fig. 1 *Structure of the inhibitor (Pectin) [6]*

The surface morphology of AZ31B-H24 Mg alloy samples of both welded and non-welded specimens was evaluated by SEM (DST FIST, ZEISS). WL measurements were performed in 1M H_2SO_4 solution at 303 K in the absence and presence of inhibitor concentrations of 1 ppm, 10 ppm, 100 ppm, 500 ppm, and 1000 ppm on non-welded and welded specimens. After soaking for 24 hours, the samples were washed with deionized water and dried under vacuum. Corrosion assessment parameters were calculated using the following formulas:

$$\text{Inhibition Efficiency, (IE\%)} = \frac{(W_m\text{-}W_n)}{W_m} X100 \tag{1}$$

where W_m = WL without inhibitor; W_n = WL with inhibitor

$$\text{Corrosion Rate, CR} = \frac{534 \text{ X Weight loss (g)}}{\text{Density (g/cm3) X Area (cm) X Time (h)}} \tag{2}$$

3. Results and Discussion

3.1 Weight Loss Measurements

WL measurements were carried out for welded and non-welded specimens of Mg alloy in 5% NaCl solution 1, 10, 100, 500, and 1000 ppm for 24 hours at 303±1K in the concentration range from 1 ppm, 10 ppm, 100 ppm, 500 ppm, and 1000 ppm. The highest concentration is sometimes limited by the solubility of the compound. If at two consecutive concentrations, the inhibitor efficiency showed no further increase, higher concentrations were not tested. A decrease in weight loss and corrosion rate as well as an increase in inhibition efficiency in the presence of an inhibitor are observed for both the specimens. The protection of Mg alloy in the NaCl medium can be attributed to the active sites like OH, double bonds, and oxygen atoms present in the pectin polymer [3]. The relative inhibition efficiencies of the compounds can be rationalized qualitatively under the assumptions that [5]:

(i) The inhibition is essentially based on the coverage of the metal surface by the inhibitor molecules, thus making the contact of the corroding species difficult.
(ii) Attachment of the molecules on the metal surface is facilitated through the coordination of π electron system to the metal atom and
(iii) The stability of the complex is somewhat related to the molecules being planar.

It is observed from Table 1 that the inhibitor protects both the welded and non-welded specimens of Mg alloy, and it also reflects that there is no significant change in the inhibition efficiency. As the concentration of the inhibitor is increased though % IE also increases at higher concentrations, the % IE is almost levelled off and only slight variation is observed. The maximum inhibition efficiency of 97.17% is achieved for welded compared to that of 96.87% for unwelded specimens.

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3.2 Adsorption Isotherm

Adsorption studies with different types of metal surfaces using organic compounds containing aromatic rings reveal that these compounds in general adsorb through a flat orientation on the metal surface. To elucidate the adsorption behavior of inhibitors, the data obtained from WL studies are used to fit the best isotherm model. Various models have been tried but only the Langmuir isotherm is found to be the suitable isotherm for AZ31B-H24/NaCl/Pectin system based on the R^2 (Regression coefficient) value which is close to unity [7]. The Langmuir isotherm can be expressed as

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{3}$$

where K_{ads} = adsorption constant, C = concentration of inhibitor, and θ = fraction of the surface covered. Fig. 2 shows the Langmuir plots of C/θ Vs. C. The relationship between the adsorption constant (K_{ads}) and the free energy of adsorption (ΔG^o_{ads}) is given below,

$$\Delta G^o_{ads} = -2.303\ RT \log (55.5\ K) \tag{4}$$

Adsorption of the inhibitor involves two types of possible interaction with the metal surface. The first one is weak undirected interaction due to electrostatic attraction between inhibiting organic ions or dipoles and the electrically charged surface of the metal. This interaction is termed physical adsorption or physisorption. The second type of interaction occurs when there is an interaction between the adsorbate and adsorbent. This type of interaction involves charge sharing or charge transfer from adsorbate to the atoms of the metal surface to form a coordinate-type bond and the interaction is termed chemical adsorption or chemisorption. From Table 2, it can be concluded that the values towards the negative side of ΔG^o_{ads} point towards that the adsorption process of the inhibitor on the AZ31B-H24 alloy surface is spontaneous. It also confirms the mixed mode of adsorption based on the values lie in the range -20 to -40 kJ mol^{-1} [8].

Table 1 *Performance evaluation of different concentrations of corrosion inhibitor of Mg alloys in 5% NaCl obtained by WL measurements at 303 ± 1 K*

Type of Specimen	Concentration (ppm)	Weight loss (g)	Surface covered (θ)	IE (%)	Rate of Corrosion (g/cm^{-2} /h^{-1})
Welded	0	0.060	-	-	0.127
	1	0.0273	0.5450	54.50	0.058
	10	0.0191	0.6817	68.17	0.040
	100	0.0094	0.8433	84.33	0.020
	500	0.0042	0.9300	93.00	0.009
	1000	0.0017	0.9717	97.17	0.004
Non-welded	0	0.067	-	-	0.141
	1	0.0268	0.6000	60.00	0.057
	10	0.0193	0.7119	71.19	0.041
	100	0.0093	0.8612	86.12	0.020
	500	0.0051	0.9239	92.39	0.011
	1000	0.0021	0.9687	96.87	0.004

Table 2 *Langmuir adsorption parameters*

Type of Specimen	Slope	K_{ads} mol lt^{-1}	$-\Delta G^o_{ads}$ kJ mol^{-1}
Welded	1.028	9217.58	33.11
Non-welded	1.033	8355.64	32.87

3.3 Surface Morphology

The surface studies for the Mg alloy specimens immersed in 5% NaCl with and without inhibitor have been examined through the SEM technique. The SEM images of specimens that are immersed in 5% NaCl solution for 24 hours with and without inhibitor at the optimum concentration (1000 ppm) for welded and non-welded specimens are shown in Fig. 3. Fig. 3a (blank) shows the nearly uniform corrosion that occurred on the metal surface in the absence of an inhibitor in a NaCl solution with cracks, pits, and holes. However, in the presence of the inhibitor (Fig. 3b), corrosion products and the extent of roughness were measured and discussed with SEM microstructure. It is important to stress that when the compound is present in the solution, the morphology of Mg alloy surface is quite different from the previous one and the specimen surfaces were smoother. The formation of a film, which is distributed randomly on the overall surface of the metal, is evident from the SEM photographs. The corroded material surface is protected and smoothed in the presence of the inhibitor. The protection of metal by the inhibitor is seen clearly in both the welded and non-welded specimens of the present Mg alloy. This is in agreement with the results reported elsewhere [9].

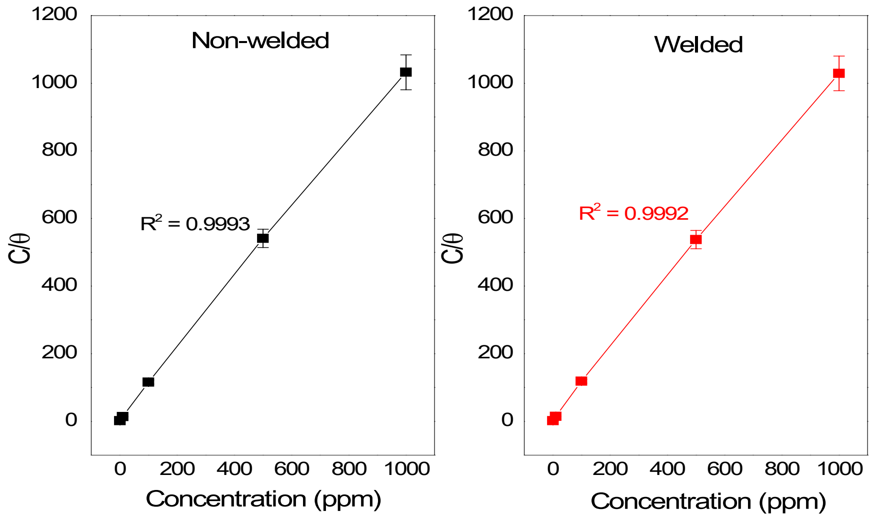
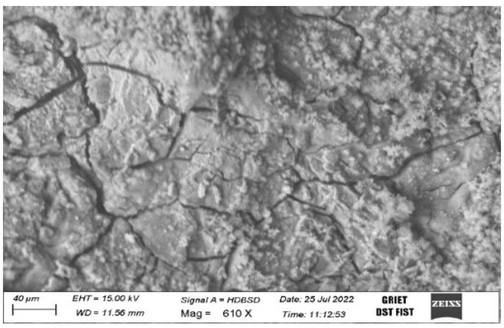
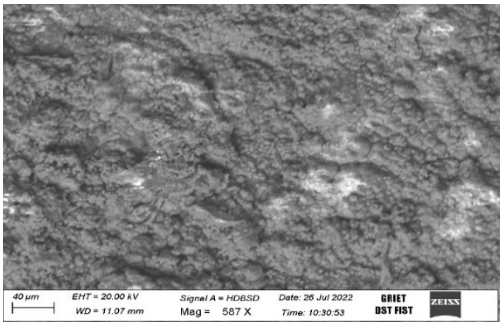


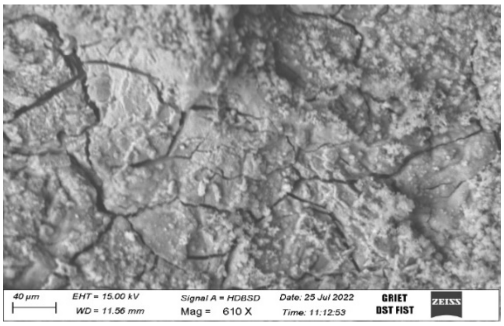
Fig. 2 *Langmuir adsorption plot*



a) Blank



b) Pectin (Welded)



c) Pectin (Non-welded)

Fig. 3 *SEM images of Mg alloy in 5% NaCl solution (a) Without inhibitor; (b) With inhibitor (Welded); (c) Non-welded specimens*

4. Mechanism of Inhibition

Based on the results of WL and SEM, the following mechanism is proposed. When the metal is immersed in 5%NaCl solution in the presence of pectin, the molecules move towards the Mg alloy and adsorb on the surface thus preventing the material [10]. Generally, organic inhibitors containing acid groups block both the cathodic and anodic sites on the metal surface. In this case, the inhibitor pectin is a water-soluble polymer and also it contains a repeating unit called pyran, in addition to that it also has heteroatoms, which adsorb on the cathodic sites and decrease the hydrogen evolution process [11,12]. Both the lone pair of electrons and double bonds adsorb on the anodic site and subsequently reduce the metal dissolution. Therefore, the mixed mode of adsorption has occurred which is revealed by the Langmuir isotherm model. In both the welded and non-welded regions of Mg alloy. The inhibitor functions similarly and it appears that there is no change in the mechanism of inhibition.

5. Conclusions

The following conclusions are drawn for the corrosion of AZ31B-H24 alloy in NaCl medium:

1. Pectin has performed well as an advantageous inhibitor against corrosion of welded and unwelded AZ31B- H24 alloys in 5% NaCl.
2. The weight loss studies revealed that the inhibitor efficiently worked to prevent the metal in the aqueous medium.
3. Langmuir adsorption isotherm is being obeyed by the pectin inhibitor for the inhibition process and the adsorption mode is mixed type.
4. Morphological study reveals the shielding of the metal surface by the inhibitor molecules.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

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