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THE CORROSION BEHAVIOUR OF ALUMINUM ALLOY 2024 - T3 IN ACIDIC ENVIRONMENTS

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ABSTRACT

This research aimed at analysing the acidic corrosion behavior of aluminum alloy 2024-T3 commonly used in the aerospace. We study the variation of corrosion rate with immersion time at different values of H_2SO_4 *concentration and corrosion rate variation depending on the concentration of the solution setting the group of corrosion of the alloy. Aluminum forms initially a few-nm-thick layer of aluminum oxide, γ-Al, which after prolonged exposure in humidified air is covered by aluminum oxyhydroxide, γ-AlOOH, and subsequently by various hydrated aluminum oxides and aluminum hydroxides. The exposed metal surfaces involved aspects of the corrosion process in 0.1M* H_2SO_4, *0.01M* H_2SO_4 *and 0.001M* H_2SO_4 *solutions, to determine the type of corrosion and propagation mechanism in acidic environments.*

KEYWORD: corrosion, aluminum alloy, corrosion rate, penetration index, pitting, sulfuric acid

1. Introduction

Aluminum is prone to pitting corrosion in the average pH near neutral, which covers virtually all natural environments, such as surface water, sea water and moist air.

Aluminum and its alloys has a natural corrosion protection from its oxide layer, but if exposed to aggressive environments it may corrode. But, if properly developed, alloys of aluminum may be reliable and have a long service life. In oxygen containing environment (air, water), aluminum is rapidly covered with a dense oxide layer. The aluminum oxide is essentially passivated, prevents corrosion, and the thickness of the layer may vary as a function of alloying elements, temperature and environment. There are many factors that may affect the stability of the aluminum oxide and thereby cause corrosion:

- the oxide is not stable in alkaline (pH > 9) or acidic (pH < 4) environments [1];
- some elements may become incorporated in the oxide and destabilize it; aggressive ions (chlorides, fluorides) may attack the oxide locally [2].

These factors lead to corrosion by pitting, which can propagate to the extent that conditions are favorable. Electrochemical corrosion mechanisms of the pitting are very complex and not fully understood. By pitting corrosion has two distinct phases: initiation and propagation.

Sulfur dioxide (SO_2) has long been considered as the most important gaseous agent in atmospheric corrosion. In the presence of atmospheric acidifying pollutants, such as SO_2, the anode reaction is facilitated and, consequently, the total corrosion rate as well. Upon deposition of SO_2, it interacts with the aqueous environment.

Pitting corrosion is observed commonly in aluminum and aluminum alloys exposed to aqueous environments. This type of corrosive attack can lead to premature failure of high-strength Al alloys used in aerospace structures. Traditionally, the fundamental cause of pitting corrosion has been attributed to local breakdown of the passive film that forms on a metal surface, resulting in subsequent dissolution of the substrate material [3, 4].

In the presence of SO_2, oxidizing agents such as O_3 and H_2O_2 may also play a role in the atmospheric corrosion of aluminum. Besides a strong humidity dependence, it is generally agreed that deposition of SO_2 has mainly been investigated through field studies and chlorides and the pH in rain are major factors that determine the corrosion rate of aluminum [5].

This work aimed at analysing the acidic environment behavior, such as of 2024 aluminum alloy commonly used in the aerospace. We investigated the variation of corrosion rate with immersion time at different values of the H_2SO_4 concentration, and corrosion rate versus the concentration of the solution and setting the group of corrosion of the alloy. Also, we studied the metal surfaces aspects exposed of the corrosion process in 0.1M H_2SO_4, 0.01M H_2SO_4, and 0.001M H_2SO_4, solutions to determine the type of corrosion and propagation mechanism in acidic environments.

2. Experimental procedure

Corrosion measurement involves the application of various techniques to determine the corrosiveness of the environment and the rate of metal loss. Corrosion measurement is usually a quantitative method of evaluating the performance and effectiveness of corrosion control and prevention techniques [6]. The corrosion penetration rate due to direct attack can usually be estimated from relatively simple laboratory test in which small samples of the related materials are exposed to a well simulated actual environment with a frequent weight change and dimensional measurements carefully taken.

The corrosion penetration rate (V_{cor}) is usually expressed in mm/yr and may be calculated as:

$$V_{cor} = \frac{\Delta m}{S \cdot t} \qquad (1)$$

where V_{cor} is the rate of corrosion penetration in mm/yr, Δm is the weight loss in milligrams; S is the exposed specific area of the specimen in square centimeter, ρ is the density of the specimen in grams per cubic centimeter and t is the exposed time in hours [7, 8].

The use of this corrosion rate expression in predicting corrosion penetration is usually successful if the environment has been properly simulated in the laboratory, and the corrosion forms homogeneous [9]. Penetration index (P) is calculated taking into account the corrosion rate and the specific weight of aluminum [10]:

$$P = (24 \cdot 365 \cdot V_{cor})/(1000\rho) \qquad (2)$$

where ρ is the specific weight, g/cm^3.

2.1. Materials and method

The weight loss technique which is a destructive method has been applied in the corrosion characterization of aluminium alloy 2024 in diluate solution of sulfuric acid 0.1M, 0.01 M and 0.001 M at a temperature of 25^0 C. Exposure time was set at one day (24 hours) to 30 days. Alloy composition is shown in Table 1.

***Table 1**. Chemical composition of aluminum alloy 2024, (% wt)*

Al	Mg	Si	Mn	Cu	Zn	V	Ni	Cr	Ti	Zr
rest	1.4294	0.0878	0.7845	4.4791	0.0422	0.0123	0.0116	0.0025	0.0289	0.1339

The materials used for this work were purchased from Universal Alloy Corporation Europe SRL. The strips of the materials were cut into coupon sizes of dimension of about 50×30×1 mm and initial surface area of about 0.0015 cm^2 followed by polishing with emery paper, degreasing with lime, washed with distilled water and dried by dabbing with filter paper.

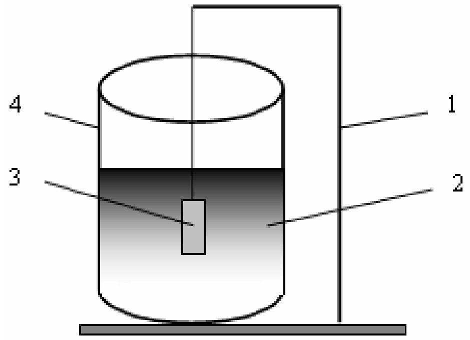

***Fig. 1.** Device setup: 1 – support; 2 – dilute H_2SO_4; 3 – sample; 4 –Berzelius glass*

Weigh the sample to four decimal electronic analytical balance (m_1), is then suspended on the support (1) (Figure 1).

Samples of each type were removed at the same time intervals, which were examined visually and microscopically.

Removal of corrosion products was performed by wiping with cotton wool soaked in distilled water, followed by washing with water and drying with filter paper and reweighing.

In the corrosive vessel was poured sulfuric acid solution at concentrations of 0.1M, 0.01M and 0.001M to 2/3 of its height. The samples was immersed in the environment corrosive rectangular aluminum plate (50x30×1 mm) and held for 14 days. The sample removed, rinsed with tap water, was distilled water, dried by dabbing with filter paper and reweighed (m_2).

Sample weight loss Δm = m_1-m_2, corrosion rate (V_{cor}) (equation 1), and penetration index P (equation 2) were calculated.

2. Results and Discussion

In table 2, the results of mass loss (Δ m) during corrosion tests, corrosion rate (V_{cor}) and penetration index (P) computed for the experimental samples are presented.

The curves corresponding to the variation in time of the corrosion rate (V_{cor}) for each of the solution concentration for the samples corrosion tested are presented in figure 2.

Table 2. *Values of mass losses, corrosion rate (V_{cor}) and penetration index (P)*

Conc. **H_2SO_4**	**Temp.** [^{0}C]	**Time** [h]	**Δm** [g]	**V_{cor}** [g/m^2·h]	**P** [mm/an]
0.1 M	25^{0}C	24	0.0015	0.000401	0.0012
		48	0.002	0.00107	0.0034
		96	0.0037	0.00396	0.0127
		168	0.0049	0.00918	0.0295
		336	0.0058	0.0217	0.0698
		672	0.0009	0.00675	0.0217
0.01 M	25^{0}C	24	0.0058	0.0015	0.0048
		48	0.0061	0.00326	0.0104
		96	0.0073	0.00782	0.0251
		168	0.0085	0.01593	0.0513
		336	0.0094	0.0352	0.1153
		672	0.00085	0.0037	0.0119
0.001 M	25^{0}C	24	0.0094	0.00251	0.0080
		48	0.01	0.00535	0.0172
		96	0.018	0.0192	0.0618
		168	0.024	0.045	0.1449
		336	0.032	0.067	0.2157
		672	0.00087	0.00652	0.0209

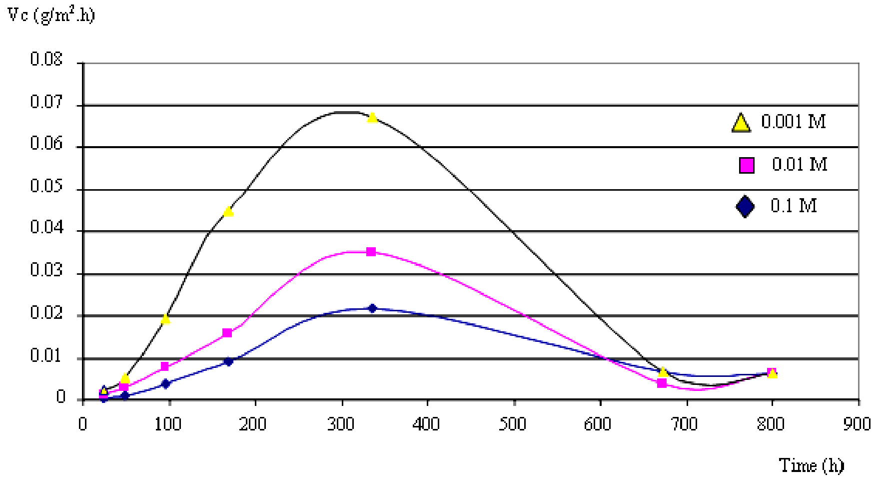

Fig. 2. *Variation of corrosion rate with immersion time at different values of concentration of H_2SO_4.*

According to Figure 2, the results indicate an increase in corrosion rate to 336hours, after which the corrosion rate decreases and stabilizes at 672hours, both for the solution of 0.1 M and 0.01M for 0.001M solution. The significant increase is recorded at 336h and 0.001M H_2SO_4 solution, the corrosion rate reaches the maximum value of 0.067g/m^2.h.

After the value of (V_{cor}) was established in the group of corrosion resistance alloy part studied and its degree of corrosion resistance (Table 3).

***Table 3.** Corrosion resistance*

Group corrosion resistance	Corrosion rate	The degree of corrosion resistance
I. Perfectly stable	0.001	1
II. Very stable	0.001-0.005	2
III. Stable	0.01-0.05 0.05-0.1	3 4
IV. Relatively stable	0.1-0.5 0.5-1.0	5 6
V. Less stable	1.0-5.0 5.0-10.0	7 8
VI. Unstable	10.0	9

After the value of (V_{cor}) in Table 2 are observed for aluminum alloy 2024 is part of the corrosion resistance (Table 3).

At the same time, it may happen that the corrosion product, ($Al(OH)_3$), formed on the metal surface of aluminum hydroxide deposits that isolates Al from contact with corrosive agents, so that the curves showing variation of corrosion rate versus time have a tendency to flattening (Figure 2).

Following the change in the corrosion rate depending on the concentration of the solution, there is an increase of low corrosion rate in solutions of dilute H_2SO_4, appreciable growth rate of corrosion taking place in the 0.001M H_2SO_4 solution (Figure 3).

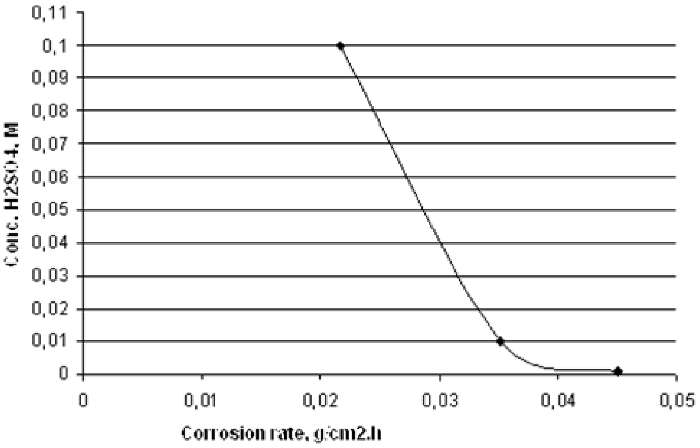

***Fig. 3.** Dependence of corrosion rate vs. solution of H_2SO_4 concentration at: 0.1M, 0.01M and 0.001M*

Following penetration index variation versus on the concentration of sulfuric acid solution is found increasing penetration index in weak diluted solutions, increasing penetration index appreciable place with 0.001M H_2SO_4 solution (Figure 4), when its value is 0.2157 (mm/year).

From the study of metal surfaces aspects of the corrosion process in solutions of H_2SO_4, 0.1 M 0.01M and 0.001M, it is found that the corrosive process is not a generalized process, but one located. Increasing the concentration of the location of the process of corrosion, corrosion is the type pitting that is more pronounced as the solution is less diluted. Corroded samples were examined under an electron microscope type Leica metallographic M2500, determining their surface microstructure, after having been processed in this aim by grinding, polishing and chemical attack with 5% orthophosphoric acid for 5 minutes.

Examination and photography was performed at a magnification of 50 times.

Figures 6 - 8 show micrographs of samples exposed to the solution of H_2SO_4 (0.1 M, 0.01 M and 0.001M), after exposure of 672 hours, where there is a localized corrosion by pitting or points.

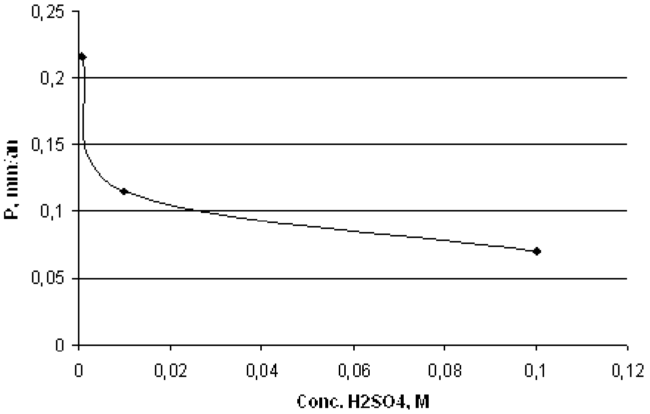

Fig. 4. *Penetration index variation of aluminum alloy 2024 in H_2SO_4 solution at different concentrations*

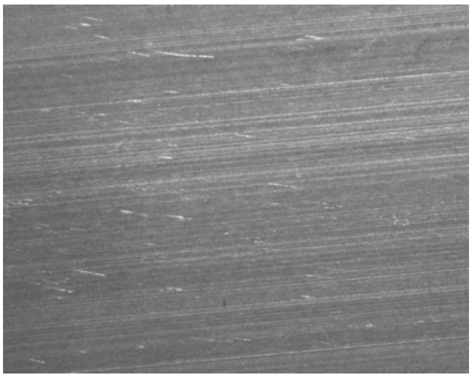

Fig. 5. *Initial sample (50×)*

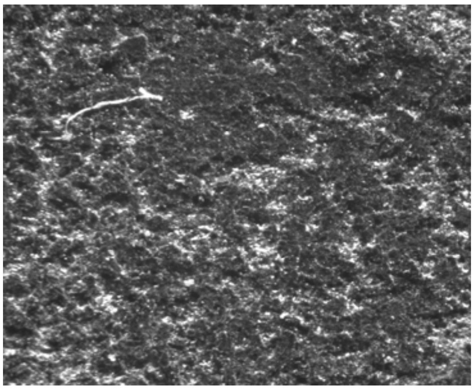

Fig. 6. *Corrosion in 0.1M H_2SO_4 solution (50×)*

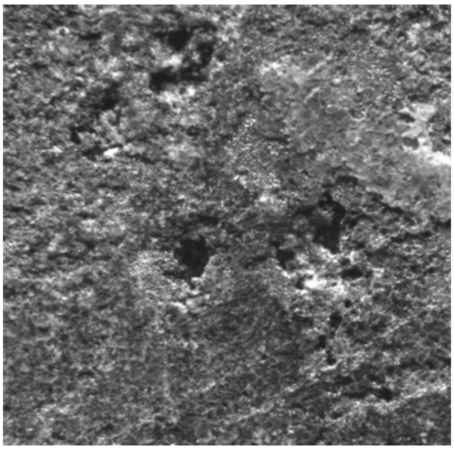

Fig. 7. *Corrosion in 0.01M H_2SO_4 solution (50×)*

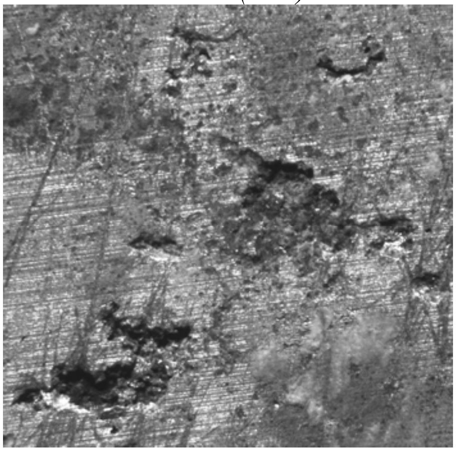

Fig. 8. *Corrosion in 0.01M H_2SO_4 solution (50×)*

According to data from Figures 6-8, aluminum dissolution by forming ions (Al^{3+}) in the bottom of pit as is observed more strongly, creates an electric field that directs ions (SO_4^{2-}) by the cavity, chemically solution neutralizing and forming aluminum sulfate. Ions (SO_4^{2-}) are the most mobile of all ions involved in these reactions.

Dissolution reaction of aluminum in dilute solutions of sulfuric acid based on the reaction (3):

$$2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2 \quad (3)$$

Hydrolysis of aluminum sulfate was according to the reaction:

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \qquad (4)$$

This will lead to the forming of pits acidification with pH <3.

The environment is very aggressive.

$Al(OH)_3$ will precipitate. Micro-bubbles of hydrogen to reduce H^+ ions will move to the surface of aluminum hydroxide where pits are formed which will form white aluminum hydroxide deposits, as it is illustrated in Figure 9, which accumulate on the bottom.

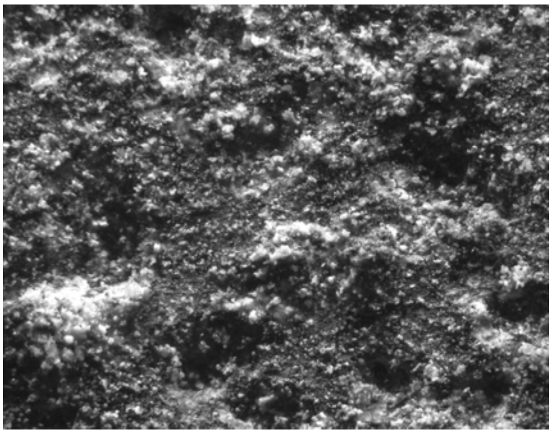

Fig. 9. *Deposits of white aluminum hydroxide (×20).*

Aluminum forms initially a few-nm-thick layer of aluminum oxide (γ-Al), which after prolonged exposure in acidic environments is covered by aluminum oxyhydroxide, (γ-AlOOH), and subsequently by various hydrated aluminum oxides and aluminum hydroxides. The stability of the compounds decreases with acidity and results in the dissolution of Al^{3+}.

Most pits stop after a few days. Polarization studies have shown that when pits stop growing, they will be repassivated.

If the alloy is polarized again, these points will not be restarted, but the pits will appear in new areas.

Conclusions

The main objective of this investigation was to study to acidic corrosion behavior of 2024 aluminum alloy. We study the variation of corrosion rate with immersion time at different values of H_2SO_4 concentration.

Corrosion rate variation depends on the concentration of the solution setting the group of corrosion of the alloy.

The exposed metal surfaces studied aspects of the corrosion process in solutions, to determine the type of corrosion and propagation mechanism in acidic environments. After the value of (V_{cor}) was established in the group of corrosion resistance alloy part studied and its degree of corrosion resistance.

Following the change in corrosion rate versus the concentration of the solution, there is an increase of low corrosion rate in solutions of dilute H_2SO_4, appreciable growth rate of corrosion taking place to the 0.001M H_2SO_4 solution. According to penetration index variation versus on the concentration of sulfuric acid solution, this is found increasing penetration index in weak diluted solutions, and increasing penetration index appreciable place with 0.001M H_2SO_4 solution, when its value is 0.2157 (mm / year).

The micrographs of samples exposed to the solution of H_2SO_4 at different concentrations and time show that there is a localized corrosion by pitting. Dissolution reaction of aluminum in dilute solutions reveals the presence of aluminum hydroxide precipitate. Micro-bubbles of hydrogen to reduce H^+ ions will move to the surface of aluminum hydroxide where pits are formed which will form white aluminum hydroxide deposits.

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