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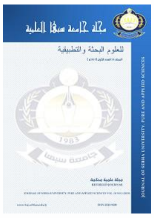

The Corrosion Inhibition Effect on Fatigue Behavior for Aluminum Alloy 5052 in the Saline Environment

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ABSTRACT

The corrosion inhibition of Al alloys is the subject of huge technological importance wing to the use of these alloys in wide industrial applications. Fatigue life (number of cycles to failure Nf) for Al-Mg alloy in 3.5% NaCl at different acidity and alkalinity and 3.5% NaCl (pH=1) with inhibitors was investigated in this study. The inhibitors were composed mainly of phosphate, adding a certain proportion of other nontoxic inhibitors to select alternatives to environmentally hazardous chromate. Fatigue behavior was studied by using the corrosion fatigue machine with plane-bending mode. The large difference between the fatigue life in the corrosive mediums, such as NaCl, and that in dry air is noticed. The results showed that in 3.5% NaCl without inhibitor, the minimum fatigue life is obtained at pH=1, where the media is too aggressive (extremely acidic), whereas the highest value is obtained at pH=5 where the very low solubility of oxide film on the alloy. As the concentration of inhibitor increased the number of cycles was increased as well. The scanning electron microscope (SEM) had conducted on the surface morphology and fracture section of the specimens for characterizing.

تأثير تثبيط التآكل على سلوك الكلل لسبيكة الألومنيوم 5052 في الأوساط المالحة

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الكلمات المفتاحية:
سبائك الألومنيوم
AA5052
تآكل
الكلل
المثبطات

الملخص

تثبيط تآكل سبائك الألومنيوم هو موضوع ذو أهمية تكنولوجية كبيرة نظراً لاستخدام هذه السبائك في تطبيقات صناعية واسعة. تمت دراسة عمر الكلل (عدد الدورات حتى الانهيار Nf) لسبيكة ألومنيوم-ماغنيسيوم في تركيز 3.5٪ كلوريد الصوديوم بدرجات حموضة وقلوية مختلفة و3.5٪ كلوريد الصوديوم (الرقم الهيدروجيني = 1) مع استخدام مثبطات. المثبطات تتكون أساسًا من الفوسفات، أضيف إليها نسبة معينة من مثبطات غير سامة أخرى لاختيار بدائل للكرومات الخطرة بيئيًا. تم دراسة سلوك الكلل باستخدام آلة إجهاد التآكل مع وضعية الثني. لوحظ فرق كبير بين عمر الكلل في الوسائط المسببة للتآكل، مثل كلوريد الصوديوم، وتلك الموجودة في الهواء الجاف. أظهرت النتائج أنه في 3.5٪ كلوريد الصوديوم بدون مثبط، يتم الحصول على الحد الأدنى من عمر الكلل عند الرقم الهيدروجيني 1، حيث كانت الوسائط شديدة العدوانية (شديدة الحموضة)، بينما تم الحصول على أعلى قيمة لعمر الكلل عند الرقم الهيدروجيني 5، حيث أن قابلية الذوبان منخفضة جدًا لطبقه الأكسيد على سطح السبيكة. مع زيادة تركيز المثبط، ازداد عدد الدورات للانهيار أيضًا. تم استخدام المجهر الإلكتروني الماسح (SEM) لدراسة سطح الكسر ومقطعه العرضي.

1. Introduction

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Aluminum and its alloys represent a significant series of materials due to their high technological value. Also, the unique integrations of properties provided by aluminum and its alloys make aluminum one of the majorities economical, versatile, and attractive metallic materials for a wide range of uses-from soft, highly ductile wrapping foil to the most demanding engineering applications. Al-Mg alloys (5xxx series), which are the strongest non-heat treatable aluminum alloy, its usage found in automotive body and components structures due to their high corrosion resistance, good strength, good formability, and weight savings. The use of AA5052, as one of the Al-Mg series, in aircraft fuel, pressure vessels, fan blades, oil lines, and tanks, miscellaneous marine and applications were good workabilities, very good resistance to corrosion, high fatigue strength, and weldability, is desired [1-4]. Aluminum has an oxide layer that represents a natural corrosion protection system, but it may corrode and break down if exposed to aggressive surrounding conditions such as in seawater that has a high concentration of chloride ions (Cl−) [5].

One of the widely used methods to control corrosion is corrosion inhibitors, especially in acidic solutions. The corrosion inhibition of Al alloys is the subject of huge technological importance wing to the use of these alloys in wide industrial applications [6-9]. A corrosion inhibitor is a substance that, when added in a little amount to an environment normally corrosive to a metal or alloy in contact with it, effectively reduces the corrosion rate. Inhibitors are widely used in neutral aqueous solutions and are particularly useful in recirculating systems, such as heating, hydraulic, and refrigerating systems [10]. The most widespread inorganic inhibitors used for Al alloys are chromates [11]. Chromates are used in kinds of corrosion prevention coatings including conversion coatings and primers. At the same time, chromate is considered the benchmark for all other corrosion inhibitors to meet so having a comparison point for chromate-free inhibitors would also be beneficial [12], [13]. There have been many research reports on natural products as corrosion inhibitors in different aggressive environments [14-16]. In fatigue tests on 7xxx series aluminum alloys many researchers have shown that fatigue crack growth rate slows down at high levels of chromate additions [17], [18].

Laboratory corrosion-fatigue tests can be classified as either cycles-to-failure (complete fracture) or crack propagation (crack growth) tests. In cycles-to-failure testing, specimens or parts are subjected to enough stress cycles number to initiate and propagate cracks until a complete fracture happened. Such data are usually obtained by testing smooth or notched specimens. However, it is difficult to distinguish between CFC (Corrosion Fatigue Cracking) initiation and CFC propagation life with this type of testing. In crack propagation testing, the crack growth rates of preexisting cracks under cyclic loading are determined by using fracture mechanics methods. Sharp defects or preexisting cracks in a material eliminate or reduce the crack initiation portion of the component fatigue life. Both types of testing are important. However, it appears that crack initiation is of more significance in the failure process of relatively thin sections, while crack growth appears to dominate thick-section component endurance [19]. In our study, a cycles-to-failure test (complete fracture) was conducted on corrosion fatigue experiments. Authors of this paper decided to study corrosion fatigue life for Al-Mg alloy 5052 in 3.5% NaCl (pH=1, 3, 5, 7, 9, and 11), and 3.5% NaCl (pH=1) with inhibitors.

2. Experimental procedure

The testing material was AA 5052 (Al-Mg) wrought alloy in O-temper (without thermal treatment) state. Specimens were cut from a hot-rolled sheet of a 5052 aluminum alloy. The test material, 5052 aluminum alloy whose chemical composition is given in Table 1 was used in all experiments in this study. Flat tensile specimens (thickness = 3 mm), having dimensions presented in Fig. 1 were used in the corrosion fatigue tests to determine the fatigue life in various environments.

Table 1: Chemical Composition of 5052 Al Alloy (wt. %).

Element	Si	Fe	Cu	Mn
Wt. %	0.1	0.26	0.029	0.081
Mg	Cr	Zn	Ti	Al
2.51	0.192	0.025	0.028	Bal.

Specimens of all tests were prepared by polishing with 280-, 400-, and finally to 1200-grit papers in succession, cleaned, degreased, and dried in air. Corrosion fatigue experiments were carried out using a plane bending fatigue testing machine shown in Fig. 2. The machine is equipped with a corrosion cell which allows the determination of the fatigue life of specimens in different environments. All experiments were done under a repeated fatigue stress cycle in which the maximum stress (σmax) and minimum stress (σmin) are not equal. They are both in tension, the ratio (R) of the minimum stress to the maximum stress was equal to 0.5, the mean stress (σm) was equal to 75 MPa (applied stress= 100 MPa) and the frequency was a constant value of 13.3 Hz (800 rpm).

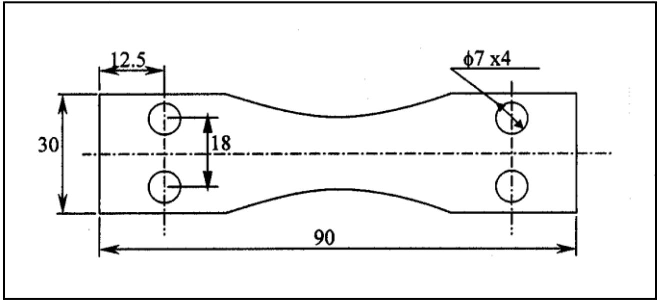

Fig. 1: Dimensions of Fatigue Test Sample, mm.

The corrosion resistance of AA 5052 was determined by the oxide film of the surface and the intermetallic phases containing Al and Mg and it exhibited the characteristic of localized corrosion in chloride media. Therefore, the chosen inhibitors should have been able to prevent (Cl ¯) from destroying the oxide film, enhance its stability, and inhibit the corrosion induced by intermetallic phases [20]. The chosen inhibitors in this study are sodium phosphate Na3PO4, sodium molybdate Na2MoO4, and sodium citrate Na3C6H5O7. Phosphate has been used to suppress the corrosion of an aluminum alloy in practice, so it was combined with other chosen inhibitors to get different kinds of compound inhibitors.

Corrosion fatigue tests were carried out in 3.5% NaCl aqueous solutions at pH = 1, 3, 5, 7, 9, and 11. Corrosion fatigue tests were conducted in 3.5% NaCl aqueous solutions at pH = 1 with the presence of previous inhibitors. The total amount of inhibiting pigments was at different concentrations (250,500,750, and 1000) ppm in the solutions.

In this study, a cycles-to-failure test (complete fracture) was conducted on corrosion fatigue experiments under a constant frequency of 13.3 Hz, stress ratio (R=0.5), and mean stress (σm) of 75 MPa. The number of cycles to failure (Nf) for each specimen was determined. The relation between (Nf) and the type and concentration of the chemical environment was investigated. Specimen surface of corrosion fatigue tests was characterized using XRD thin film (Panalytical Xpert Pro), optical microscope and scanning electron microscope (Jeol-5410, Japan) to examine the surface morphology of specimens and their fracture mechanisme.

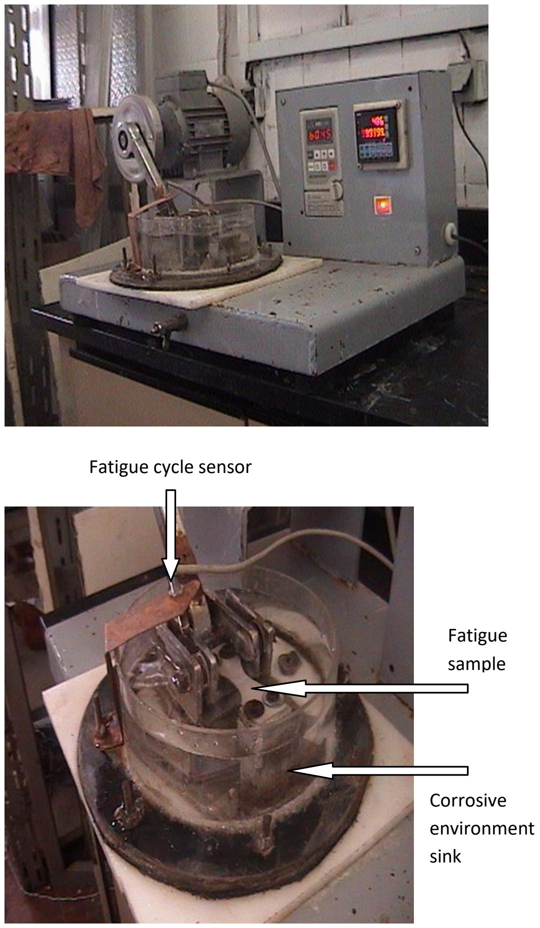

Fig.2 Plane-bending Fatigue Testing Machine.

3. Results and discussion

The fatigue strength of the investigated alloy (5052 Al-Mg wrought alloy in O-temper) in the air at 5x108 cycles is 110 MPa [1]. Therefore, the fatigue life of the alloy at maximum applied stress (100 MPa) is also 5x108. The maximum fatigue life in 3.5%NaCl solution at the same applied stress was at condition, pH=5 (174307 cycles). There is a big difference between the number of cycles to failure obtained for the alloy in the air to that obtained in 3.5%NaCl. This behavior is consistent in all the specimens. Therefore, a large decrease in the number of cycles to fail the material has occurred at the corrosive mediums. After fatigue tests in 3.5% NaCl solution at different pH, the fatigue lives of AA5052 were determined. As a general rule, the protective film is stable in aqueous solutions in the pH range of 4.5-8.5 whereas it is soluble in strong acids or alkalis leading to a rapid attack of aluminum [21]. The various forms of aluminum oxide all exhibit minimum solubility at about pH 5, [22]. Fractographic analysis was performed on failed specimens to help determine the controlling mechanisms of failure. Fractography provides information such as the nature and location of the critical discontinuity, as well as the apparent trends in the corrosion shapes, features, and damage severity [23]. Fig.3 shows SEM images of the fracture section for fatigue specimen at 3.5%NaCl (pH=1), where the lowest cycles to failure. They show the fatigue crack initiation, and rough surface due to corrosion attacks which lead to high-stress concentration then fatigue crack initiation, therefore crack propagation, and finally the failure of the material.

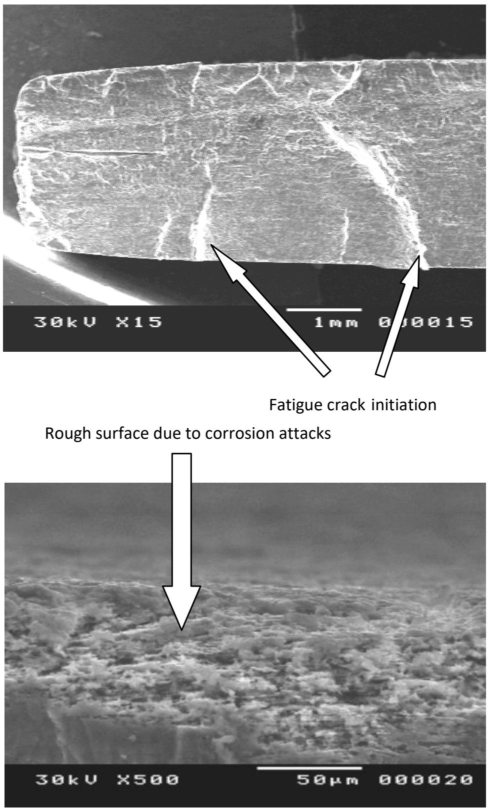

Fig.3 SEM Fracture Section at 3.5%NaCl (pH=1).

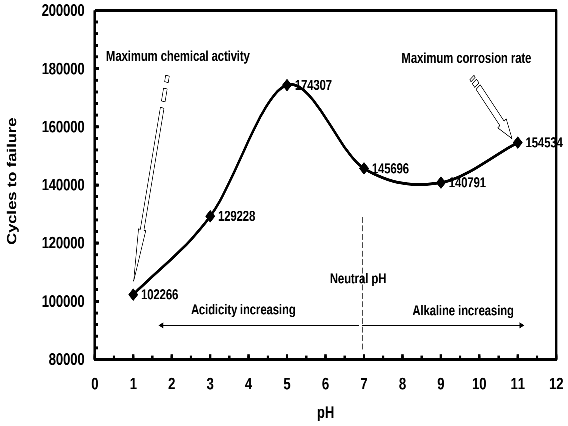

Fig.4 Effect of pH Solution (3.5%NaCl) on Fatigue Life for Alloy 5052.

Fig.4 shows the relation between fatigue life and the pH of the testing environment, without an inhibitor, (3.5% NaCl). It is shown that the highest number of cycles (174307 cycles) is obtained at pH=5 where the oxide film on aluminum has very low solubility, pH (4 - 9) due to low chemical activity (passivity).

On the other hand, the lowest number of cycles (~ 102266 cycles) is obtained at pH=1 where the media is so aggressive (extremely acidic) due to maximum chemical activity and this is emphasized as shown in Fig.4, Fig.5.

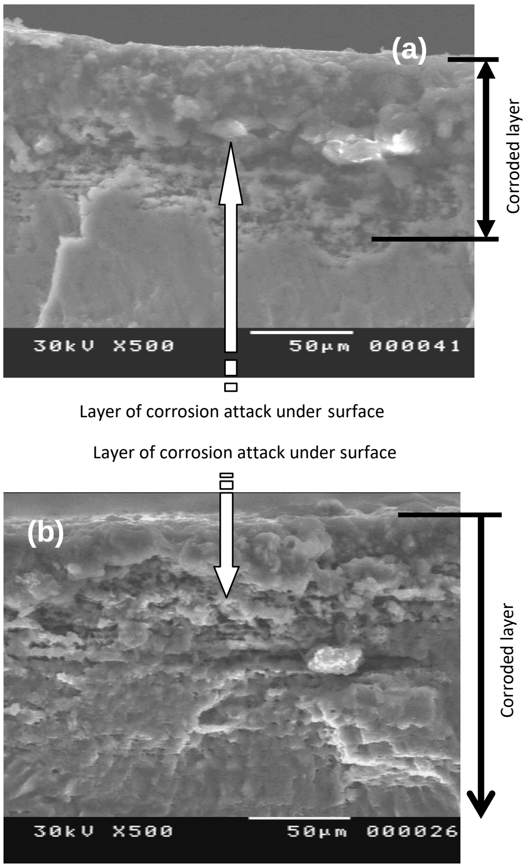

Fig.5 SEM of Fracture Surface Section at 3.5%NaCl (a) pH=5 and (b) pH=1.

Inhibitors added to the blank solution (3.5%NaCl) at (pH=1, minimum fatigue life in Fig.4). From Fig.6, it is clear that the addition of (Na_3PO_4 & $Na_2Cr_2O_7$) to the testing environment (3.5% NaCl) at pH=1 enhanced the fatigue life to a marked extent (156270 cycles at 1500 ppm, in comparison to 102266 cycles obtained for the blank at the same condition pH=1). In corrosion fatigue failures there is usually a large area covered with corrosion products and a smaller roughened area resulting from the final brittle fracture [24] as shown in Fig.7.

The fatigue life of the aluminum alloy in 3.5% NaCl with inhibitor composed from (Na_3PO_4 & Na_2MoO_4) ratio (4:1). In general all concentrations give good fatigue life, but the best fatigue life was at 500 ppm (143184 cycles). It is observed from the fig.8 that when the inhibitor contains phosphate, molybdate, and citrate ratio (8:1:1) added to the testing environment of 3.5% NaCl (pH=1), the fatigue life of the alloy increased as the concentration of the inhibitor increased. Thus, it was 121451 cycles at 250 ppm and became 142847 cycles at 1000 ppm.

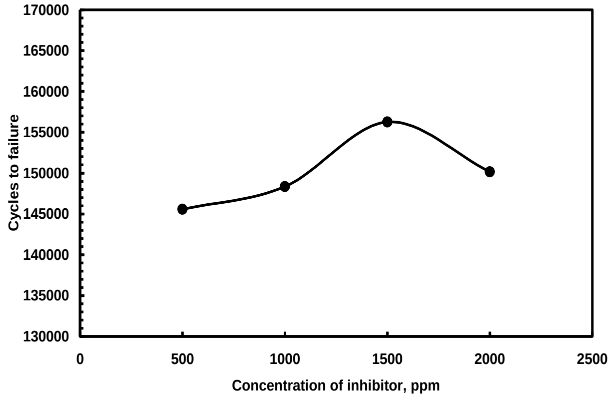

Fig.6 Effect of Inhibitor Addition (Na_3PO_4 & $Na_2Cr_2O_7$) Ratio (1:1) to 3.5% NaCl (pH=1) on Fatigue Life.

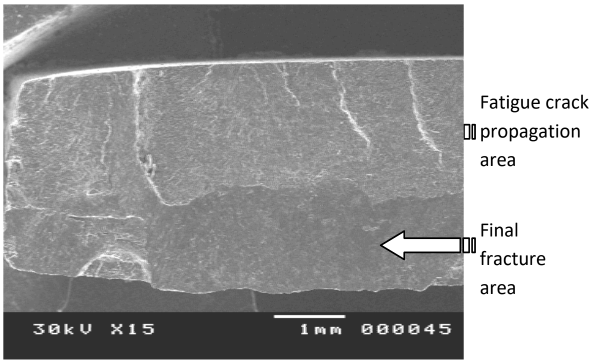

Fig.7 SEM Fatigue Fracture Section at ($Na_2Cr_2O_7$) Addition (250 ppm) to 3.5% NaCl.

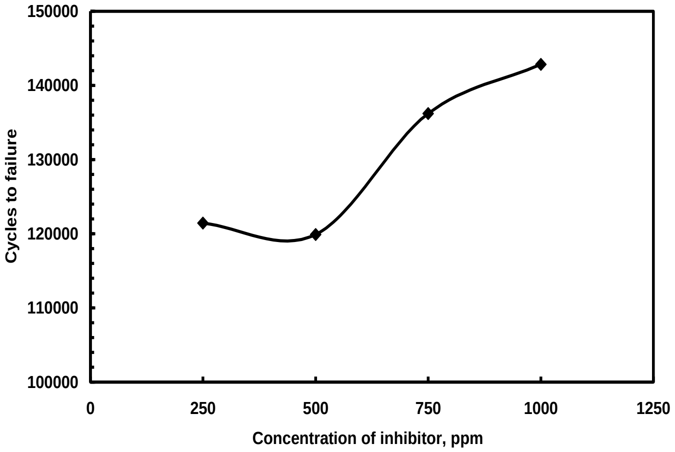

Fig.8 Effect of Inhibitor Addition (Na_3PO_4 & Na_2MoO_4 & $Na_3C_6H_5O_7$), ratio (8:1:1) to 3.5% NaCl (pH=1) on Fatigue Life.

Corrosion of AA5052 in 3.5%NaCl solution was induced mainly by Cl^- ions and the potential difference between the matrix and intermetallic phases. If the inhibitors in the solution could retard these reaction processes, they would be able to inhibit the corrosion of the aluminum alloy [18].

The main protection of phosphate is to react with corrosion products that deposit on the surface of the metal and form a protective film.

For the aluminum alloy in 3.5% NaCl solution with phosphate, phosphate could react with Al^{3+} and Mg^{2+}, which can result from the hydrolysis of the oxide layer and localized corrosion induced by the intermetallic phases and form the deposition film on the surface to further inhibit propagation of the hydrolysis and galvanic couple corrosion. However, the processes occurred only after metal cations appeared in the solution; therefore, the inhibition of phosphate cannot occur in a short time [20]. **Molybdate** can act as an oxidizing inhibitor and reinforce the surface passivating film of the aluminum alloy, so it is difficult to ingress chlorides into the aluminum surface layer. As a result, a small amount of pitting and localized corrosion occurs [20]. **Carboxylates** in general provide the combined action of an easily-reduced cation and a strongly-adsorbed anion that forms a chemical bond between the carboxyl ion and the metal substrate. **Citrate** has three carboxyls, which have been used as an inhibitor for pitting corrosion of aluminum alloys. It combines with phosphate to inhibit corrosion of the aluminum alloy. They adsorb on the surface of the aluminum alloy instead of the chloride ion with competitive adsorption to reduce the rupture probability of the oxide film [20].

4. Conclusion

From the presented study the following conclusions can be drawn:

1- The fatigue life of aluminum alloy 5052 is largely differing based on the corrosive mediums, such as NaCl, or dry air.

2- In 3.5% NaCl solutions, the maximum fatigue life of 5052 was at pH 5 (174307 cycles), and the minimum fatigue life was at pH 1 (102266 cycles).

3- Addition of inhibitors usually improves the fatigue life by small percentages.

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