تـــأثير بعض العــوامل على ســـلوك تـــآكل ســـبيكة ألومنيوم- نحاس في المحاليل المائية لبعض الأحماض غير العضوية

إعداد

سها بنت طلال الغول

بحث مقدم لنيل درجة الماجستير في الكيمياء

كيمياء فيزيائية

إشراف

أ.د. سناء طاهر عرب

د. احترام عبدالله نور

كلية العلوم
جامعة الملك عبد العزيز
جدة- المملكة العربية السعودية

صفر 1431هـ - فبراير 2010م (22-2-1431هـ)

قائمة المحتويات

المستخلص

تمَّت دراسة تأثير بعض العوامل (تركيز الحمض و درجة حرارة المحلول و إضـــافة مُثبِّط) على سلـــــوك تآكـــــل سبيـــكـــة ألومنيوم–نحاس في المحاليـــل المائيـــــة لـــكـــــل من HCl وH_3PO_4 و H_2SO_4 و ذلك باستخدام طرق القياس الكيميائية (طريقة قيـــاس: حجـــم الهيدروجين المتصاعد وطريقة الفقد في الوزن) و طرق القياس الكهروكيميائية (طريقة قياس: أطياف المعاوقة الكهروكيميائية و الاستقطاب عند جهد ديناميكي)، كما أمكن دراســـة البنيـــة المجهرية للسطح عند ظروف معملية مختلفة و ذلك بتطبيق تقنية المسح الإلكتروني المجهري.

بصفة عامَّة، أفادت النتائج أنَّ معدل تآكل سبيكة الدراسة يزداد بزيادة كل من تركيـــز الحمض و درجة حرارة المحلول، حيث حُسبت و نُوقشت الثوابت الديناميكية الحرارية لتآكـــل سبيكة الدراسة ($E^{\#}_{app}$ و $\Delta H^{\#}$ و $\Delta S^{\#}$) عند تراكيز مختلفة لكل حمض قيد الدراســـة. كمـــا اتفقت نتائج القياسات المختلفة على أنَّ معدل تآكل سبيكة الدراسة في الأحماض المختلفة عنـــد نفس الظروف من التركيز و درجة الحرارة يتبع الترتيب التالي:

$$H_2SO_4 < H_3PO_4 < HCl$$

و لقد تمَّ تعزيز الترتيب السابق بدراسة التصوير المجهري لسطح سبيكة الدراسة عنـــد نفـــس الظروف حيث أظهر حمض HCl تآكل نقري شديد لسطح سبيكة الدراسة بينما أظهر كل مـــن حمض H_3PO_4 و H_2SO_4 خصائص أقل عدائية.

و لمَّا كان حمض HCl يُظهر تآكلاً شديداً لسبيكة الدراسة عند الظروف المختلفة فـــإنَّ الدراسة تضمنت تأثير إضافة مُثبِّط للحد من معدل تآكل سبيكة الدراسة في محلول 0.5N مـــن حمض HCl ، حيث استخدم المستخلص المـــائي لأوراق الريحان كمثبط طـــــبيعي (AEBL) وآمن. دلَّت نتائج القياسات الكيميائية أنَّ مثبط الدراسة فعَّال و آمن و ذلك في مدى التركيز من $0.05\ g\ L^{-1}$ إلى $2.5\ g\ L^{-1}$ بينمـــا يُصنَّـــف من المثبطـــات الخطـــرة عند تركيز أقـــل مـــن $0.05\ g\ L^{-1}$، وبناءاً على نتائج قياسات الاستقطاب أمكن تصنيف مثبط الدراسة كمثـــبط مـــن النوع المهبطي والذي يعمل على إعاقة العملية المهبطية. و بدراسة شكل سطح سبيكة الدراسة في غياب ووجود كمية متزايدة من المثبط، لُوحظ وجود تثبيط ملحوظ لكل من التآكل العـــام و التآكل التثقيبي. وكما أنَّ فعالية التثبيط المستنبطة من القياسات الكيميائية تزداد بزيادة التركيـــز وفقاً لنموذج تمكين للامتزاز عند درجة حرارة ثابتة بينما تلـــك المســـتنبطة مـــن القياســـات الكهروكيميائية فتتغير مع التركيز وفقاً لنموذج لانجمير، و بتتبع تغير فعالية التثبيط مع درجـــة الحرارة لُوحظ نقصاً ملحوظاً في فعالية التثبيط بزيادة درجة الحرارة مصحوباً بطاقة تنشـــيط مرتفعة مقارنة بطاقة التنشيط المرصودة للوسط غير المُثبَّط ممَّا يدلُّ علـــى حـــدوث امتـــزاز

فيزيائي لدقائق المثبط على سطح السبيكة، و عليه تمَّ الربط بين مكونات المثبط و خصـــائص التثبيط عند الظروف المدروسة.

Abstract

The effect of some factors (acid concentration, solution temperature and inhibitor addition) on the corrosion behaviour of Al-Cu alloy in aqueous solutions of HCl, H_3PO_4 and H_2SO_4 was studied by using chemical (hydrogen evolution, HE, and Weight Loss, WL) and electrochemical (electrochemical impedance spectroscopy, EIS, and potentiodynamic polarization, PDP) measurements. SEM technique was used to evaluate the microstructure of the alloy surface under different conditions.

In general, the obtained data revealed that the corrosion rate of the studied alloy increases as both acid concentration and solution temperature increase. Moreover, various thermodynamic parameters ($E^{\#}_{app}$, $\Delta H^{\#}$ *and* $\Delta S^{\#}$) for Al-Cu corrosion were estimated at different concentrations of the studied acids and well discussed. However, at certain acid concentration and solution temperature, the corrosion rate of Al-Cu alloy in the studied inorganic acids can be given in the following order:

$$H_2SO_4 < H_3PO_4 < HCl$$

SEM images for Al-Cu alloy surface in the studied acids at the same conditions confirmed well the previous order.

Since HCl solutions showed severe attack on the studied Al-Cu alloy, the addition of inhibitor to such solutions is required to reduce and control the corrosion rate. So, the effect of aqueous extract of Basil leave (AEBL) on the corrosion behaviour of Al-Cu alloy in 0.5N of HCl was investigated. Chemical study revealed that AEBL is effective inhibitor at concentration range of 0.05-2.5 g L^{-1} while it acts as accelater at concentrations < 0.05 g L^{-1}. PDP measurements indicated that AEBL inhibit Al-Cu corrosion in 0.5 N of HCl by retarding the cathodic reactions and they can be classified as cathodic type corrosion inhibitor. SEM images for Al-Cu surface in the in absence and presence of increasing amount of AEBL emphasized that the addition of inhibitor inhibits both the general and pitting corrosion. Temkin adsorption isotherm gave the best fitting to the experimental data obtained from chemical study while Langmiur adsorption isotherm gave the best fitting to that obtained from electrochemical study. However, the studied inhibitor loses its effectiveness with increasing solution temperature with an activation energy more than that of the uninhibited solution which leads to suggest that the inhibitor adsorbed physically on the metal surface. Good correlation between AEBL constituents and its inhibitory action was obtained and discussed

SUMMARY

The present study was carried out to investigate the corrosion behaviour of Al-Cu alloy in solutions of three inorganic acids namely HCl, H_3PO_4 and H_2SO_4 under the influence of some factors, e.g. acid concentration, solution temperature and the addition of natural inhibitor. The study was achieved by using chemical (hydrogen evolution, HE, and weight loss, WL) and/or electrochemical (electrochemical impedance spectroscopy, EIS, and potentiodynamic polarization, PDP) measurements. Surface morphology of the studied alloy was examined under different experimental conditions.

The thesis consists of three chapters.

CHAPTER (I)

General introduction deals with the following subjects:

- Aluminum and it's alloys
- Aluminum-copper phase diagram
- Corrosion behaviour of aluminium
- Methods of corrosion protection
- Corrosion inhibition
- Previous studies on the corrosion of aluminium and its alloys in aqueous solutions of some inorganic acids
- Previous studies on the corrosion inhibition of aluminum and its alloys in aqueous acid solutions by using natural inhibitors

CHAPTER(II)

The experimental details deal with the materials, chemicals, solutions, instruments and methods of measurement used in the present study.

CHAPTER (III)

Results and discussion which is divided into three main parts as follows:

PART (1)

In this part, the effects of different concentrations of HCl, H_3PO_4 and H_2SO_4 on the corrosion behaviour of Al-Cu alloy at 30°C were studied by using HE, WL, EIS and PDP measurements. The surface morphology of the studied specimen after immersion for 120 min in acid solutions of certain concentration (0.5M) was examined. The obtained results can be summarized as follows:

- **HE** and **WL** studies revealed that the corrosion rate of Al-Cu alloy increases with an increase in acid concentration (in the studied range of concentrations) except in the case of H_2SO_4 as it was observed that irregular trend for the corrosion rate and the acid concentration. The latter result was interpreted on the basis of film dissolution or film growth under the influence of relative solution humidity.
- **EIS** study showed that the electrochemical processes on the Al-Cu alloy in the various acidic solutions can be simulated by the equivalent circuit **$R_s(Q_{dl}\ R_{ct}\ (LR_L))$** except the two cases of 6.0 and 10.0 M of H_3PO_4 where the best equivalent circuit was in the form **$R_s(Q_{dl}\ R_{ct})$**. In general, it was found that both R_{ct} and R_L decreases while Q_{dl} increases with an increase in acid concentration.
- **PDP** study proved that both cathodic an anodic curves of Al-Cu alloy were shifted to higher corrosion current density (i_{corr}) with increasing the concentration of the studied acids, indicating that the corrosion rate of the studied alloy is proportional to the acid concentration and this result was confirmed by the estimated i_{corr} values.
- All applied methods for corrosion rate measurements give the same trend for Al-Cu corrosion rate with the studied acid concentration except that the irregular behaviour of corrosion rate with H_2SO_4 concentration was not the case in the electrochemical data. However, all measurements agree well that at certain concentration of the studied acids, the corrosion rate of Al-Cu alloy gives the following order:

$$H_2SO_4 < H_3PO_4 < HCl$$

- SEM images for the Al-Cu alloy surface after immersion for 120 min in 0.5M of each studied acid emphasized the above order.

PART (2)

In this part, the effects of temperature on the corrosion behaviour of Al-Cu alloy in HCl, H_3PO_4 and H_2SO_4 solutions of different concentrations was investigated by using HE, WL, EIS and PDP measurements. The surface morphology of the studied specimen after immersion for 120 min in acid solutions of certain concentration (0.5M) was examined at two different temperatures. The obtained results can be summarized as follows:

- Chemical and electrochemical studies showed that at certain concentration of HCl, H_3PO_4 and H_2SO_4, increasing temperature leads to a systematic increase in the corrosion rate of Al-Cu alloy obeying Arrhenius relationship.

- An interesting behaviour was observed at relatively high temperatures when Al-Cu alloy was corroded in concentrated solutions of H_3PO_4 and H_2SO_4. This was the growth of porous film as indicated from the impedance spectra. So, various electrochemical equivalent circuits were uses to simulate the processes on the alloy surface depending on the acid type, its concentration and solution temperature.
- At certain concentration and different temperatures, the corrosion rate of Al-Cu alloy in the studied acids gives the following order:

$$H_2SO_4 < H_3PO_4 < HCl$$

- SEM images showed that at certain acid concentration the surface morphology of Al-Cu alloy depends on the acid type and solution temperature.
- Various thermodynamic parameters ($E^*_{app.}$, ΔH^* and ΔS^*) for the corrosion of Al-Cu alloy in the studied acids were estimated from HE and WL data.
- It was found that both $E^*_{app.}$ and ΔH^* for the corrosion of Al-Cu alloy in the studied acids have positive values, indicating the occurrence of endothermic reactions. The trend by which $E^*_{app.}$ and ΔH^* values vary with acid concentration was acid type dependence.
- The negative values of ΔS^* for studied alloy, corrosion indicated that the corrosion mechanism involves the formation of an activated complex requires association rather than dissociation which leads to more order system.

PART (3)

In this part, the effects of some factors (inhibitor concentration, temperature and immersion time) on the efficiency of aqueous extract of basil leaves(AEBL) as inhibitor to reduce the corrosion rate of Al-Cu alloy in 0.5N HCl by using chemical study and/or electrochemical study and SEM image for Al-Cu surface. The obtained results can be given as below:

- It was observed that AEBL is effective inhibitor at concentration range of 0.05-2.5gL^{-1} while it acts as dangerous inhibitor at concentration < 0.05gL^{-1} by using chemical study.
- **SEM** image**s** of Al-Cu surface in the absence and presence of increasing amount of AEBL emphasized that the addition of inhibitor inhibits both the general and pitting corrosion.
- It was remarked that AEBL inhibit Al-Cu corrosion in 0.5N of HCl by retarding the cathodic reaction and they can be classified as cathodic type corrosion inhibitor by using PDP study.
- It was found that there was agree between the **HE** and **WL** studies especially when we used 0.05 gL^{-1} inhibitor.
- The different in the immersion time of the Al-Cu alloy in the chemical and electrochemical measurements showed a difference in the effectiveness of inhibition.
- Temkin adsorption isotherm gave the best fitting to the experimental data obtained from chemical study while Langmiur obsrption isotherm gave the best fitting to that obtained form electrochemical study.

- It was suggested that the inhibitor adsorbed physically of the metal surface because it loses the effectiveness with increasing temperature with an activation energy more than that of the uninhibited solution.
- A correlation between the inhibition efficiency and its constituents was obtained and discussed.

(لايوجد ملخص عربي-لاتوجد خاتمه)

Abstract

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