J. King Saud Univ., Vol. 20, *Eng. Sci.* (1), pp. 61-68, Riyadh (2008/1429H.)

Electrochemical Characterization of Heat Treated Steel

Abdulaziz Al-Ghyamah and Maher Alodan
Chemical Engineering Department, College of Engineering,
King Saud University, Riyadh 11421, Saudi Arabia
alodan@ksu.edu.sa

(Received 29 March 2006; accepted for publication 19 February 2007)

Keywords: Heat treatment, Corrosion, Nitriding, Carburizing, EIS.

Abstract. Different steel alloys of tool steel and alloy steel were heat treated with different heat treatment processes such as hardening, gas carburizing, and gas nitriding. The electrochemical behavior, especially corrosion characteristics, of the different steel grades were evaluated using different electrochemical techniques in 0.1 M sodium chloride solutions at different values of solution pH. Potentiodynamic scans indicated similar corrosion behavior between the different heat treatment processes. However, the nitriding process added extra corrosion resistance to certain steel alloys which included strong nitride forming elements. Also, the electrochemical impedance spectroscopy and salt spray tests confirmed the same and indicated an increase in corrosion resistance after the nitriding process.

Introduction

Heat treatment is a combination of heating and cooling operations, timed and applied to a metal or alloy in a way that will produce the desired mechanical properties. Steel can be heat treated to produce a great variety of microstructures and properties (Avner, 1974; Prabhudev, 1993; Thelning, 1984; Krauss, 1990). The aim of this study was to evaluate the effect of different heat treatment processes, nitriding, carburizing and hardening, on the corrosion characteristics of different steel alloys. Nitriding is a case hardening process in which the chemical composition of the surface is changed by the addition of nitrogen. The effectiveness of the process depends on the formation of nitrides in steel by the reaction of nitrogen with the strong nitride-forming elements such as aluminum, chromium, vanadium and molybdenum (Townsend, 2000). The nitrided case consists of two distinct zones, outer and inner layers. The outer layer consists of nitrides of different elements including iron, while the inner layer consists of nitrides precipitates due to solubility limits. The thickness of the two layers depends on process time, temperature and atomic nitrogen concentration near the surface (Dingremont *et al.*, 1995; Borges *et al.*, 1997). Carburizing, also a case hardening, is used to increase the hardness and wear resistance of components, which are required to possess fairly good impact strength and resistance. Carburization process is performed by adding carbon to the surface of steel at relatively higher temperature (austenite temperature). In general, the carburized outer layer of steel is hypereutectoid steel while the core is hypoeutectoid steel. Gas nitriding and carburizing are well known processes in steel industry and more details can be found in (Prabhudev, 1993; Thelning, 1984).

The effect of heat treatment on corrosion characteristics has been studied for several years. Eight-year atmospheric corrosion tests of (UNSK12040) weathering steel were conducted in industrial, marine and rural environments for two types of heat treatment processes; quenching-and-tempering and normalizing. The results of these tests indicated that the heat treatment had no effect on the corrosion resistance (Ailor, 1971). Duplex treatments consisting of plasma nitriding and ion plating with titanium nitride were investigated by cyclic polarization scan in sodium chloride solution and by

Table 1. Chemical composition of the investigated steels

		Chemical composition %					
Group	**Designation**	**C**	**Cr**	**Ni**	**Mo**	**Mn**	**Si**
A	AISI 1035	0.32-0.38				0.6-0.9	
B	En 36	0.12-0.18	0.6-1.1	3-3.75		0.3-0.6	0.1-0.35
C	AISI 4140	0.38-0.43	0.8-1.1		0.15-0.25	0.75-1.1	0.15-0.3

subjecting samples to salt spray. These treatment improved the corrosion resistance of construction steel (X45NiCrMo4) and hot working steel (X38CrMoV5-1), but for stainless steel samples the duplex treatment led to a loss in corrosion resistance (Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens, Standard Method G-88, Annual ASTM Standards). It has been reported that for sintered steel samples, which were nitrocarburized at different temperatures and times, the thickness of the compound layer increased with the nitrocarburizing temperature and time, thus improving the corrosion resistance that was measured using potentiodynamic polarization approach (Totik, 2006). The presence of the nitride layer increases the corrosion resistance of the material, not only as a consequence of its nature and thickness, but also due to the nitrides layer formed around some of the open pores. Different specific grades of steel have been studied for different surface coatings such as phosphating. It was found that heat treatment and the type of cooling media directly affect the corrosion resistance of the substrates (Totik, 2006; Oh, Joo and Kim, 2005). It was found that heat treatment can alter and modify the localized properties using Kelvin probe to measure the Volta potential of the surface (Atık, Yunker and Merıc, 2003).

Nevertheless, there are no final conclusions about the effect of heat treatment on the corrosion resistance of steel due to the large range of process parameters and the large number of steel alloys. The purpose of this study was to investigate the influence of various heat treatments processes on the corrosion resistance of three different types of steel, AISI 1035, En36 and AISI 4140 by different electrochemical methods and salt spray testing.

Experiments

Sample preparation

Steel specimens, 10 mm diameter and 10 cm long cylinders, were used for the electrochemical and the salt spray tests. After heat treatment, all samples were cleaned with iso-propanol and acetone solutions to remove oils. Then the samples were washed with distilled water and then etched with diluted HCl solution to remove scale products and finally the samples were washed with distilled water again. Table 1, shows the three main groups of steel that were used is this study. Group A was mainly plain carbon steel. The most significant alloying elements in group B were Ni (3-3.75%) and Cr (0.6-1.1%). Group C was AISI 4140 that is a chromium-molybdenum, medium carbon steel and used as guide pins for plastic injection molds after nitriding.

Testing methods

- *Electrochemical tests:* Each steel grade with different heat treatment processes, hardening, carburizing and nitriding was subjected to several electrochemical tests. Three main electrochemical tests were conducted for each sample. First, the open circuit potential was monitored over a period of 30 minutes in the different test solutions (see below). Then, potentiodynamic scans were collected in which the sample was biased cathodically at –0.5V, then the potential was scanned at a rate of 1 mV/sec until an anodic potential of +1.5 V vs. open circuit potential was reached. This test was designed to determine the overall corrosion profile for a metal-electrolyte system over the potential range. The third electrochemical test was the electrochemical impedance spectroscopy (EIS) measurements. EIS tests were designed to indicate the differences in corrosion rates and also to observe any layer formation on top of the surface that might increase the corrosion resistance (Bäck, Nazarov and Thierry, 2005). The initial and final frequencies for the EIS tests were 100,000 and 0.01 Hz, respectively, while the AC voltage amplitude was 10 mV around the open circuit potential. The test solution used for the electrochemical experiments was 0.1 molar sodium chloride at different pH levels (4 and 9 using either HCl or NaOH to adjust the solution pH).
- *Salt spray test:* Salt spray tests were performed to evaluate the performance of heat treated steel for

outdoor exposure. The temperature of the salt spray chamber was set at 50°C, the spray solution was 5% NaCl and the test period was 30 days. The samples weight were measured before exposure after 15 days, and at the end of the test. At the end of the test, the corrosion products were removed mechanically by a bristle brush to remove loosely attached corrosion products, and then were cleaned electrochemically using 5% w/w H_2SO_4 solution plus a corrosion inhibitor at 65°C. The applied cathode current density was 200 mA/cm^2 for 3 minutes (Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens, Standard Method G-88, Annual ASTM Standards). This cleaning procedure was sufficient to remove all corrosion products and leave the underneath metal without attack.

Results and Discussion

The main results of the electrochemical behavior of hardened, nitrided and carburized samples compared with untreated samples will be discussed. It was found that the behavior of carburized and hardened samples was very similar to the untreated steel as observed by the open circuit potential values and polarization measurements as shown in Figs. 1 to 6. The open circuit potential of the hardened and untreated samples were stable and reached steady state after 20 minutes. The values of the open circuit were around -0.65 V (vs. SCE), while the open circuit potential of the nitrided samples, especially groups B and C, decreased from the initial value (-0.25 V vs. SCE) to about –0.5 V vs. SCE after 20 minutes immersion.

The results of potentiodynamic scans for all samples are shown in Figs. 1 to 6 at different pH values (in 0.1 M NaCl). At pH 4 and 9, heat treatment had a small effect on samples from group A as indicated by the potentiodynamic scans. The corrosion rates of groups A, B and C were calculated by Tafel extrapolation and are listed in Table 2 for the different pH. In the table, both corrosion currents and the resulting calculated corrosion rates are listed.

In the case of group B, the alloy exhibited better corrosion characteristics than alloy A. Also, nitrided samples indicated smaller corrosion rates and stronger passivation characteristics in alkaline solutions (pH 9). Group C also indicated small variations between the different heat treatment processes. However, at alkaline pH, Fig. 6, the nitrided surface had slightly better corrosion characteristics. In general, the results indicated that for groups B and C, the nitriding heat treatment process decreased the corrosion rates and improved the passivation behavior, especially in alkaline solutions when compared with other heat treatment processes. The reduction in corrosion rate might be attributed to the presence of nitriding alloying elements such as Cr, Ni and Mo, while this was not observed for group A. Nevertheless, the reduction in the corrosion rate due to the nitriding process was not significant as in the case of vanadium steel alloys (Borges, Rocha, Martnelli, Cabral, Klein and Franco, 1997).

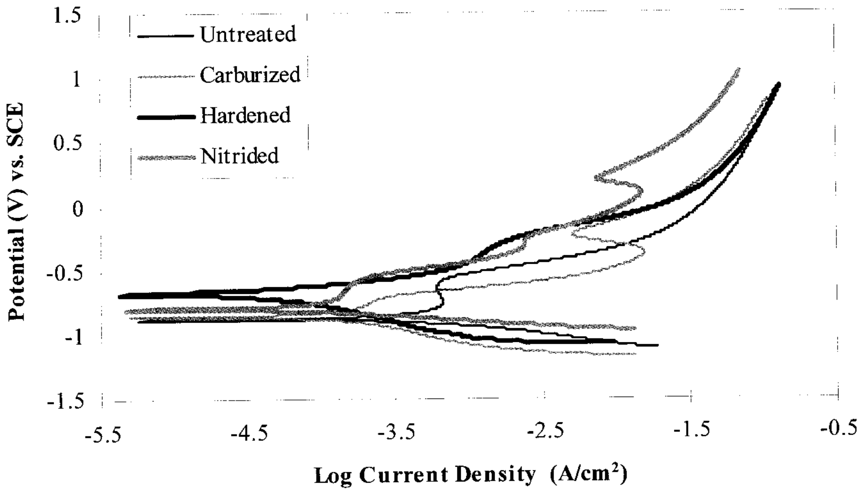

Fig. 1. Potentiodynamic scan results for group A at pH 4.

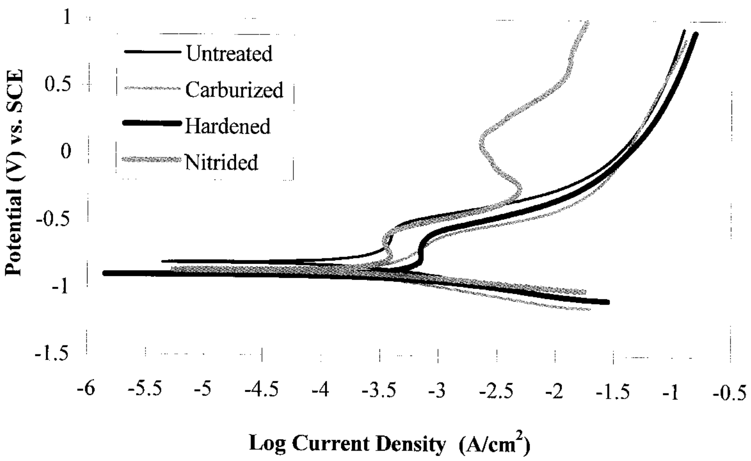

Fig. 2. Potentiodynamic scan results for group B at pH 4.

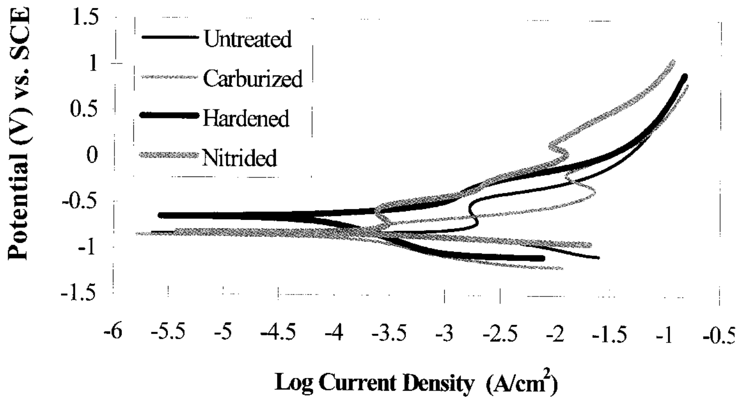

Fig. 3. Potentiodynamic scan results for group C at pH 4.

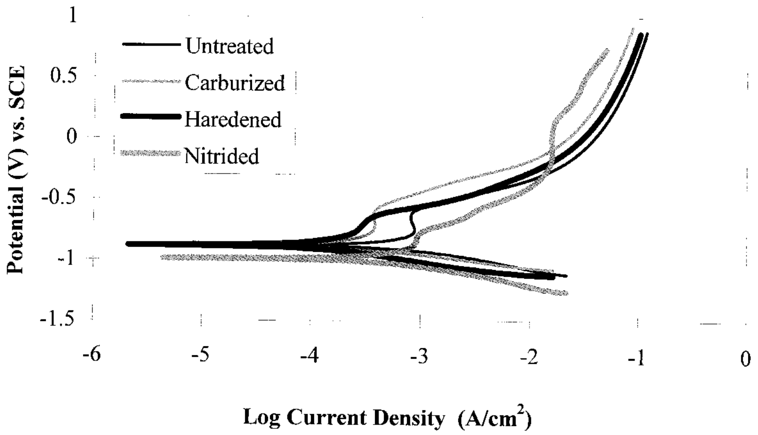

Fig. 4. Potentiodynamic scan results for group A at pH 9.

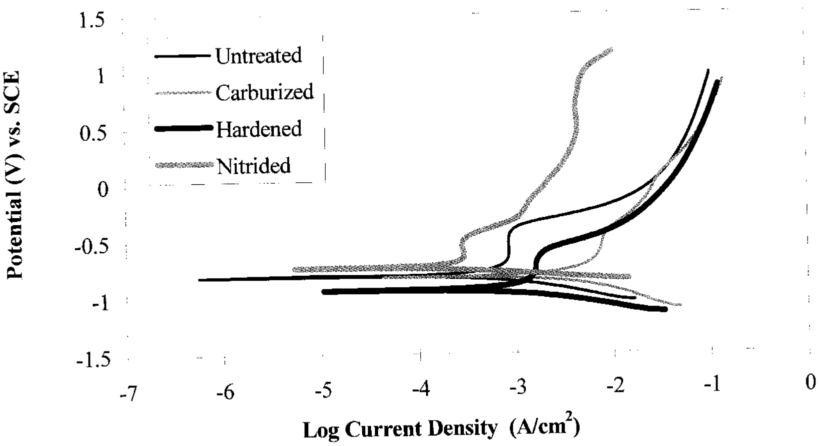

Fig. 5. Potentiodynamic scan results for group B at pH 9.

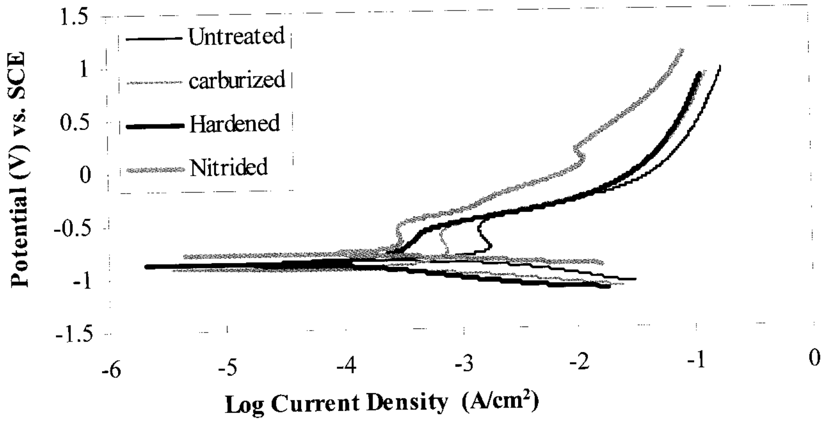

Fig. 6. Potentiodynamic scan results for group C at pH 9.

Table 2. Corrosion rates and current of steel samples by the different techniques

#	Type of Heat Treatment	Corrosion Rate, by Potentiodynamic Scan Test and Tafel Extrapolation				Salt Spray Result
		pH 4		pH 9		
		µA/cm²	Mpy	µA/cm²	mpy	mpy
A1	Untreated	1.06	0.49	5.65	2.58	53.69
A2	Carburizing	7.14	3.26	10.9	4.98	25.98
A3	Hardening	4.97	2.27	8.66	3.95	40.92
A6	Nitriding	7.44	3.40	7.65	3.49	24.89
B1	Untreated	8.82	4.03	1.79	0.81	23.55
B2	Carburizing	6.19	2.83	17.7	8.09	71.64
B3	Hardening	5.79	2.65	6.48	2.96	57.96
B6	Nitriding	5.54	2.53	4.14	1.89	28.18
C1	Untreated	6.10	2.78	25.2	11.52	50.29
C2	Carburizing	19.2	8.75	7.7	3.52	53.01
C3	Hardening	8.91	4.07	6.71	3.06	51.77
C6	Nitriding	2.76	1.26	4.68	2.13	38.69

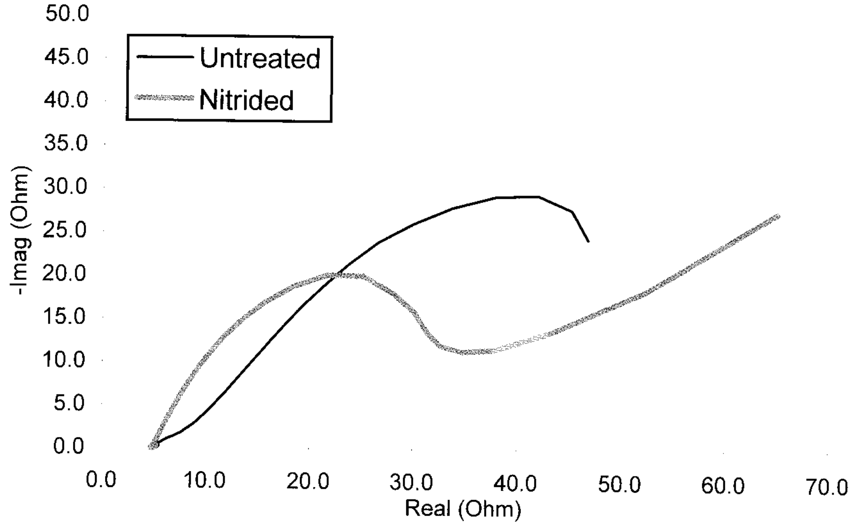

Fig. 7. Nyquist plot of raw and nitrided samples from group B.

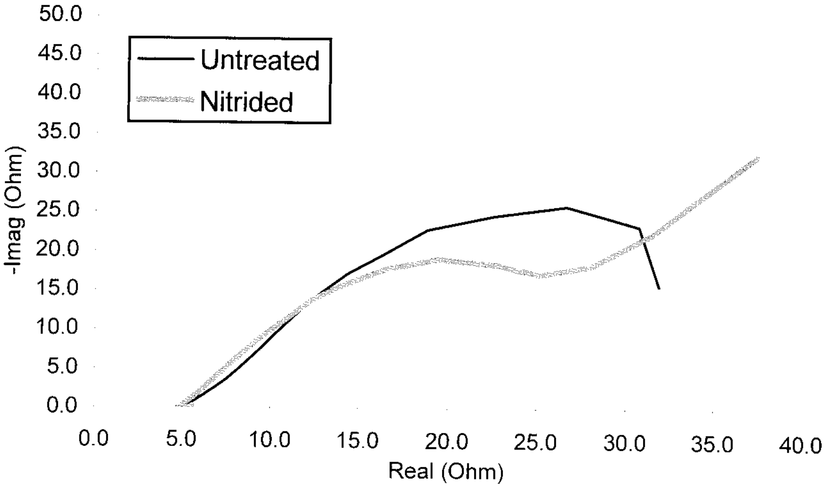

Fig. 8. Nyquist plot for raw and nitrided samples from group C.

Electrochemical impedance spectroscopy tests were performed to evaluate the corrosion resistance of the samples surface at the OCP. It was found that the behavior and shape of the spectra were similar for all types of heat-treated steel except in the case of nitrided steel. The spectra of nitrided steel exhibited two time constants, i.e. two semicircles, as shown in Fig. 7. This was observed only for group C and group B and was not observed for group A. This behavior may indicate the presence of a porous layer (i.e. the nitirded layer). The added resistance is small as indicated by the spectra indicating that the thickness of the nitrided layer is small, which was observed during the nirtiding process itself. Further studies are required to evaluate and characterize the thickness of the nitride layer by the EIS to understand its mechanism in improving the corrosion resistance.

Salt spray tests were performed to characterize the alloys behavior in accelerated atmospheric corrosion conditions. The corrosion rates were calculated based on samples weight change over 30 days exposure period which are listed in Table 2. Nitrided samples from group B and group C had good corrosion resistance compared with other heat treatment processes. In general, the corrosion rate in the salt spray chamber was higher than the corrosion rate in the electrolyte conditions due to the different nature of the two tests. During salt spray exposure, it was observed that the nitrided samples had more pronounced pitting corrosion while other samples suffered uniform corrosion. This pitting behavior can be attributed to the presence of the nitrides layer which increases the passivation characteristics as indicated by the polarization data.

Conclusions

The following conclusions can be drawn from this study:

1. In general, heat treatment processes have slight effect of the corrosion characteristics of steel types that were studied in this work. These processes include carburizing and hardening.
2. Nitriding increases the corrosion resistance of steels studied in this work that contain nitride forming elements such as Ni, Cr and Mo. Nitriding of other types of steel had little effect on corrosion resistance. EIS indicated the presence of porous layer, which leads to better characterization of the "white layer".
3. As indicated by the EIS, the presence of a protective white layer suggested that nitrided steel surface suffers from pitting corrosion more pronouncedly rather than uniform corrosion as in the case of untreated steel samples.

Acknowledgements. The authors would like to acknowledge the support of Saudi Arabian Basic Industries Company (SABIC) and the Research Center at the College of Engineering for their support.

References

Ailor, W. H. *Handbook on Corrosion Testing and Evaluation.* John Wiley & Sons, Inc., (1971).

Atik, Enver; Yunker, Umut and Meric, Cevdet. "The Effect of Conventional Heat-treated and Bronzing Zone on Abrasive Wear and Corrosion of SAE 1010, SAE 1040, DZ and 304 Steels." *Tribology International*, Vol. 36, (2003) 155–161

Avner, S. H. *Introduction to Physical Metallurgy.* 2nd ed., McGraw-Hill, (1974), 249 p.

Bäck, G.; Nazarov, A. and Thierry, D. "Probing of Atmospheric Corrosion of Metals." *Corrosion*, Vol. 61, No. 10, (2005).

Borges, P.; Rocha, J.; Martnelli, A.; Cabral, F.; Klein, A. and Franco, C. "Microstructure and Corrosion Behavior of Plasma-nitro Carburized Sintered Steel." *Advances in Powder Metallurgy and Particulate Materials*, Vol. 2, (1997), 179-190.

Dingremont, N.; Bergmann, E.; Hans, M. and Collignon, P. "Properties of Duplex Coatings Prepared by Plasma Nitriding." *Surface and Coatings Technology,* Vol. 76-77, (1995), 218-224.

Oh, K.-T.; Joo, U.-H. and Kim, K.-N. "Effect of Surface Corrosion and Dispersant on Wear." *Corrosion,* Vol. 61, No. 7, (2005).

Krauss, G. *Heat Treatment and Processing Principles.* ASM International, (1990), 281 p.

Prabhudev, K. H. *Handbook of Heat Treatment of Steels.* Tata McGraw-Hill, (1993), 18 p.

Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens, Standard Method G-88, Annual ASTM Standards.

Thelning, K. E. *Steel and Its Heat Treatment.* 2nd ed., Butterworths, (1984), 227 p.

Totik, Yasar. "The Corrosion Behavior of Manganese Phosphatic Coatings Applied to A1SI 4140 Steel." *Surface & Coatings Technology,* Vol. 200, (2006), 2711–2717.

Townsend, H. E. *Corrosion*, Vol. 56, (2000), 883-886.

دراسة كهروكيميائية للحديد المعالج حراريًّا

عبدالعزيز الغيامة، وماهر عبدالله العودان
قسم الهندسة الكيميائية، كلية الهندسة،
جامعة الملك سعود، الرياض ١١٤٢١،
المملكة العربية السعودية
alodan@ksu.edu.sa

(قدم للنشر في ٢٩/٠٣/٢٠٠٦م؛ وقبل للنشر في ١٩/٠٢/٢٠٠٧م)

ملخص البحث. يهدف هذا البحث إلى دراسة تأثير بعض عمليات المعالجة الحرارية والسطحية مثل الكربنة، والنتردة، والتقسية على الخواص الكهروكيميائية لبعض سبائك الحديد. تم تقييم تآكل هذه السبائك وتصرفها الكهروكيميائي باستخدام المحلول المائي لملح الطعام بتركيز ٠,١ مولار عند ظروف مختلفة من الرقم الهيدروجيني. دلت نتائج البحث على تشابه الأنواع المدروسة للمعالجة الحرارية من ناحية نتائج التآكل، لكن عملية النتردة أدت إلى زيادة مقاومة التآكل في سبائك معينة للحديد.

Kingdom of Saudi Arabia

Ministry of Higher Education

King Saud University

DEANSHIP OF LIBRARY AFFAIRS

THE JOURNAL OF KING SAUD UNIVERSITY

1-(Biannual): Arts- Educational Sciences & Islamic Studies - Administrative Sciences - Engineering Sciences-Science-Agricultural Sciences.
2- (Annual): Computer & Info. Sciences - Languages & Trans. - Architecture & Planning

Method of Payment: 1- Cash: At King Saud University Libraries Building 27
2- Cheque: In the name of **King Saud University library** accounts.
3- Drafts: Saudi American Bank, King Saud University branch. Account No. (2680740067-code no. 501). A copy of the draft should be Faxed to the address given below.

Annual Subscription Rates:

1- In the Kingdom S.R 20.00
2- Outside the Kingdom US $ 10.00 or equvilant for all journals except:
   a) Architecture and Planning.
   b) Computer and Information Sciences
   c) Languages and Translation. For these, subscription rates are:
      S.R 10.00 inside Kingdom
      US $ 5.00 out side the Kingdom

All correspondences should be addressed to: University Libraries – King Saud University, P.O.Box 22480, Riyadh 11495 Tel: +966 1 4676112 Fax: +966 1 4676162
E-mail: libinfo@ksu.edu.sa Web site :www.ksu.edu.sa

--✂ --cut here

Subscription Form Date: / /200

Name:...
Organization:..................................
Address:...P.O.Box:.....................
Zip code:.................
City:.......................State:..............................Tel:......... ....
Fax:....................... E-mail:..

Specific issue(s):..Number of copies( )

Payment: ☐ Cash ☐ Cheque ☐ Draft
Subscription: ☐ New subscription ☐ Renewal of subscription
Period of Subscription: ☐ 1 year ☐ 2 years ☐ 3 years
☐ 5 years ☐ more.......

المملكة العربية السعودية
وزارة التعليم العالي
جامعة الملك سعود
عمادة شؤون المكتبات

مجلة جامعة الملك سعود

١- **نصف سنوية** : الآداب – العلوم التربوية والدراسات الإسلامية – العلوم الإدارية – العلوم الهندسية – العلوم – العلوم الزراعية.

٢- **سنوية** : علوم الحاسب المعلومات – اللغات والترجمة – العمارة والتخطيط.

طريقة الدفع: ١- نقداً بمقر عمادة شؤون المكتبات– مبنى ٢٧ – جامعة الملك سعود.

٢- شيك مصدق باسم (عمادة شؤون المكتبات – حساب الخدمات) يرسل إلى العنوان البريدي الموضح أدناه.

٣- حوالة أو إيداع على (حساب الخدمات رقم ٢٦٨٠٧٤٠٠٧٦ الرمز ٥٠١) البنك السعودي الأمريكي – فرع جامعة الملك سعود – الرياض ، وترسل صورة الحوالة أو الإيداع المختومة على الفاكس الموضح أدناه أو على العنوان البريدي.

قيمة الاشتراكات: الاشتراك السنوي داخل المملكة (٢٠) ريالاً سعودياً ، وخارج المملكة (١٠) دولارات أو ما يعادلها لجميع فروع مجلة جامعة الملك سعود ماعدا فروع (العمارة والتخطيط–علوم الحاسب والمعلومات–اللغات والترجمة) اشتراكها السنوي داخل المملكة (١٠) ريالات سعودية وخارج المملكة (٥) دولارات أو ما يعادلها.

جميع المراسلات على العنوان الآتي: عمادة شؤون المكتبات – جامعة الملك سعود – الرياض ١١٤٩٥ ص.ب ٢٢٤٨٠ هاتف ٤٦٧٦١١٢ (++٩٦٦-١) فاكس ٤٦٧٦١٦٢(++٩٦٦-١) E-mail: libinfo@ksu.edu.sa موقع جامعة الملك سعود www.ksu.edu.sa

✂-----------------✂-------------------✂-------------------✂---------------✂ قص هنا

قسيمة اشتراك بمجلة جامعة الملك سعود

تاريخ تعبئة القسيمة(بالتاريخ الميلادي): / / ٢٠٠ م

ملحوظة مهمة : لضمان وصول المجلة إليكم يرجى تعبئة الخانات المسبوقة بعلامة ❖

اسم المشترك(رباعي)❖ : .... اسم الجهة (للجهات الحكومية) : ....

العنوان❖ : .... صندوق البريد❖ : .... الرمز البريدي❖ : ....

المدينة❖ : ....الدولة❖ : .... الهاتف❖ : .... الفاكس : ....

البريد الإلكتروني : ....

اسم المجلة المطلوب الاشتراك فيها : .... عدد النسخ : ( ).

طريقة الدفع: ☐ نقداً ☐ شيك مصدق(مرفق) ☐ حوالة (مرفق صورة مختومة)

نوع الاشتراك: ☐ اشتراك جديد ☐ تجديد اشتراك ☐ اشتراك فردي ☐ اشتراك حكومي

مدة الاشتراك: ☐ لمدة سنة ☐ سنتان ☐ ثلاث سنوات ☐ خمس سنوات

☐ أخرى..