The Susceptibility of 7020 Al-alloys to Pitting Corrosion at Various Heating Temperatures

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Abstract

The present work is aimed to investigate the effect of heat treatments variables (temperature & time holding) on the tendency of high strength Al-alloys type 7020.

The experiments were carried out by heating the specimens at different temperatures (100, 150, 200, 250, 300, 350, 400, 450 and 500 °C) for two periods of holding time, one and two hours.

Polarization technique was used to study the effects of microstructures on their electrochemical behavior in 3.5 % NaCl solution.

Microscopic & X- ray examination had been used to reveal pitting corrosion on the microstructure of non heated and heated 7020 Al-alloys .

The results refer to as temperatures of heat treatment increase from 100-500°C pitting corrosion appears on the precipitated phases.Pitting corrosion tendency increase with increasing temperature of heating. Increase time holding of heat treatment from 1 hr. to 2 hrs would increase the pitting corrosion.

Introduction

Pitting is a deleterious form of localized corrosion and it occurs mainly on metal surfaces which owe their corrosion resistance to passivity. The major consequence of pitting is the breakdown of passivity, i.e. pitting, in general, occurs when there is breakdown of surface films when exposed to pitting environment(1-5).

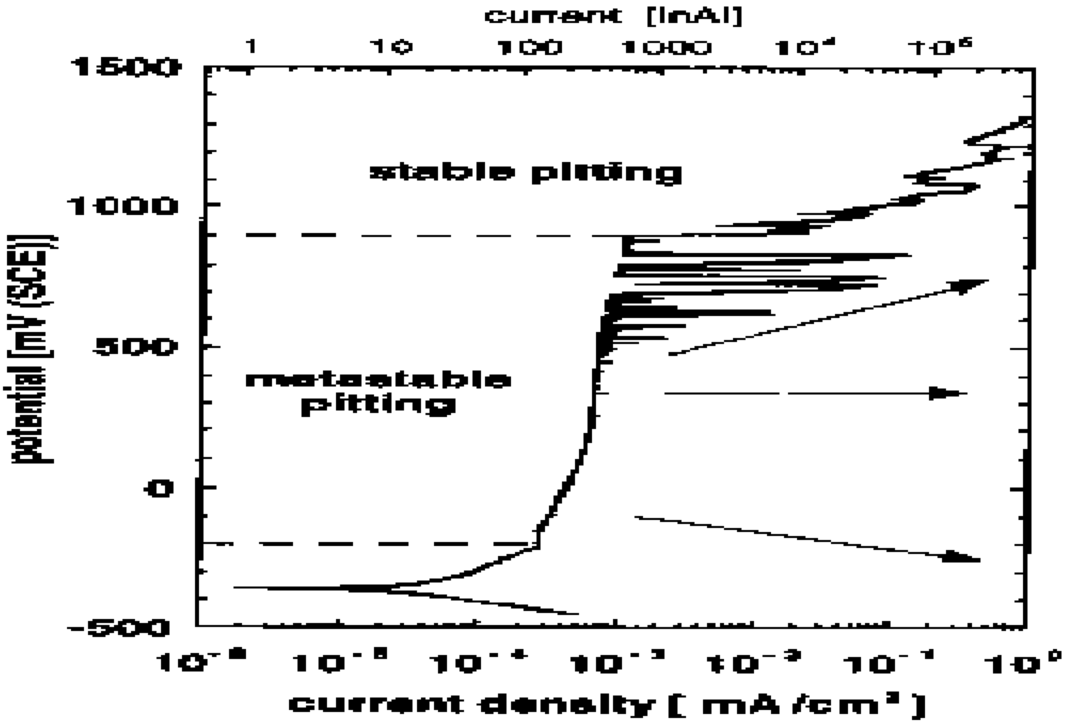
Many engineering alloys, such as stainless steels and aluminum alloys, are useful only because of passive films, which reduce the rate of corrosion of these alloys.

Classical pitting corrosion caused by passive film breakdown will only occur in the presence of aggressive anionic species, and chloride ions are consider one of these species because many metal actions exhibit considerable solubility in chloride solutions (6,7). Chloride is a relatively small anion with a high diffusivity; it interferes with passivity, and it is ubiquitous as a contaminant.

Pitting can be considered to consist of various stages: passive film breakdown, metastable pitting, pit growth(7). Any of these stages may be considered to be the most critical.

Metastable pits are typically considered to be those of micron size that initiate and grow for a limited period before repassivating Fig.(1).

Metastable pits can form at potentials far below the pitting potential (which is associated with the initiation of stable pits) and during the induction time before the onset of stable pitting at potentials above the pitting potential(9). Metastable pits initiate and grow for a period at potentials well below the pitting potential (7), which provides evidence in contradiction to the definition of the pitting potential as being the potential above which pits initiate.



Metastable pits can form at potentials far below the pitting potential (which is associated with the initiation of stable pits) and during the induction time before the onset of stable pitting at potentials above the pitting potential(7,8). Metastable pits initiate and grow for a period at potentials well below the pitting potential (2,8), which provides evidence in

Fig. (1) Typical potential current curve of stainless steel in Cl^- showing the different stages of localized corrosion. (3)

Large pits, which would be considered to be stable by any criterion, can stop growing or die. If the conditions (environment and potential) at the dissolving wall of a pit are not sufficiently aggressive, the pit will repassivate. The potential at the pit bottom is lower than that at the outer surface as a result of the ohmic potential drop associated with current flow out of the pit. As the pit deepens, the ohmic path length and ohmic resistance increase. This tends to cause an increase in the ohmic potential drop, a decrease in the local potential, and a decrease in the pit current density**(8)**. The environment tends to be acidic and rich in chloride, owing to hydrolysis of the dissolved metal cations and electrolytic migration of chloride into the pit. The high concentration in the pit is depleted by transport out of the pit but is replenished by continued dissolution at the pit bottom, As the pit deepens, the rate of transport out of the pit decreases, so the pit can be stable with a lower anodic current density replenishing the environment **(7).**. As mentioned previously, the pit current density tends to decrease with time, owing to an increase in the pit depth and ohmic potential drop. Repassivation might occur if a sudden event, such as loss of a pit cover, caused a sudden enhancement of transport and dilution of the pit environment to the extent that the rate of dissolution at the pit bottom would be insufficient to replenish the lost aggressive environment **(2).**

Fig.(2) shows that a stable pit starts growing at the pitting potential E_P, where the current increases sharply from the passive current level and, on reversal of the scan direction, repassivates at E_R, where the current drops back to low values representative of passive dissolution. Corrosion experts generally consider that materials exhibiting higher values of E_P and E_R are more resistant to pitting corrosion, and cyclic polarization experiments are commonly used for this purpose. Furthermore, pits did not initiate at potentials below this limiting E_R, even after very long times**(4,8).**

For instance, it is common to use the term breakdown potential (E_b) for the initiation potential of localized attack because one is not always sure if the form of this attack is pitting, crevice corrosion, or intergranular corrosion, or if the current increase is the result of general transpassive dissolution. The pitting potential is sometimes referred to as the pit nucleation potential, E_{np}, and the repassivation potential is sometimes called the protection potential, E_{prot}.

Pits almost always initiate at some chemical or physical heterogeneity at the surface, such as inclusions, second-phase particles, solute-segregated grain boundaries, flaws, mechanical damage, or dislocations **(9)**. Most engineering alloys have many or all such defects, and pits will tend to form at the most susceptible sites first. Pits in stainless steels are often associated with MnS inclusions, which are found in most commercial steels. The role of MnS inclusions in promoting the breakdown and localized corrosion or stainless steels has been recognized for some time. **(8)** Recent improvements in alloy production have led to steels with lower sulfur content to improve pitting resistance.

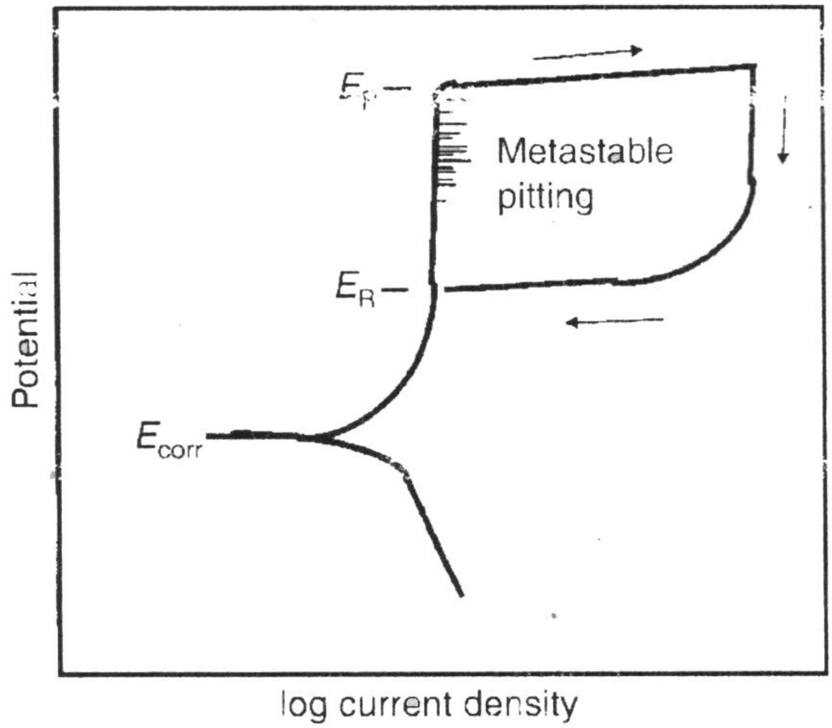


Fig.(2) Schematic of a polarizaition curve showing critical potentials and metastable pitting region . E_P, pitting potential; E_R, repassivation potential; E_{corr}.corrosion potential (9).

The tendency of metals or alloys to pitting corrosion depends mainly on the microstructure and chemical compos ion. It was found**(9-11)**
that pitting potential for Al-Zn-Mg-Cu alloys were more negative than that for high purity aluminum. Also it is observed**(11)** that , the addition of Mg to (Al – Cu) alloys improves corrosion resistance and E_{corr} shifts to more noble direction. Al – Zn – Mg alloy depot with 0% , 0.01% , 10.05% and 0.1% by weights of tin were prepared to determine(12) the effect of tin anode efficiency in the environment . The different microstructures of the Al – Zn – Mg – Sn alloy evolved were correlated with the anode

efficiencies. The result obtained showed that the anode efficiency of Al – Zn – Mg – Sn alloy increased with Tin concentration. pit nucleation and propagation takes place in the zones where intermetallic particles are accumulated. Muller and Galvele (13,14) observed that the aged Al-Cu alloys were susceptible to intergranular corrosion which, they attributed to the precipitation of second phase particles. Wesisshans et al found(14) that, the aged specimens were more susceptible to pitting corrosion that the solution treated ones. Moreover, annealed and cold worked alloys presented more negative pitting and repassivation potentials than those submitted to age hardening with direct or interrupted quenching(15).

Experimental & Procedure Work

Aluminum alloy type 7020 had been used in this work with chemical composition compared with standard condition of 7020 AL- alloys are shown in Table (1). The chemical composition analysis was carried out by using Spectrometer .Dv.4, This analysis was done in the Institute of Specialized Engineering.

Table (1) The chemical composition of 7020 alloy

Elements	Standard value (1)	Measured value
Si	< = 0.35	0.121
Fe	< = 0.40	0.290
Cu	< = 0.20	0.200
Mn	0.05 - 0.5	0.0764
Mg	1 -1.5	1.25
Cr	0.10 - 0.35	0.228
Zn	4 - 5	4.56
Ti	0.08	0.0319
Al	BALANCE	BALANCE

Specimens of (25x30) cm were cut from the metal plate .The surface to be tested have (25x25) cm.

Nine treatments achieved in electrical furnace type GARBOLITE – SHEFFIELD-ENGLAND +15°C with maximum of 1200°C in the following form :-

1. Heat treatment (H.T) No.1 homogenization treatment at 100°C for 1hr & 2hrs and cooled in furnace.
2. Heat treatment (H.T) No.2 homogenization treatment at 150°C for 1hr & 2hrs and cooled in furnace.
3. Heat treatment (H.T) N0. 3 homogenization treatment at 200°C for 1hr & 2hrs and cooled in furnace.

4. Heat treatment (H.T) No.4 homogenization treatment at 250°C for 1hr & 2hrs and cooled in furnace.
5. Heat treatment (H.T) No.5 homogenization treatment at 300°C for 1hr & 2hrs and cooled in furnace.
6. Heat treatment (H.T) No.6 homogenization treatment at 350°C for 1hr & 2hrs and cooled in furnace.
7. Heat treatment (H.T) No.7 homogenization treatment at 400°C for 1hr & 2hrs and cooled in furnace.
8. Heat treatment (H.T) No.8 homogenization treatment at 450°C for 1hr & 2hrs and cooled in furnace.
9. Heat treatment (H.T) No.9 homogenization treatment at 500°C for 1hr & 2hrs and cooled in furnace.

The surface specimen is ground with abrade paper of grades (400 - 800 - 1000 & 1200) respectively .The grinding process was continued until the clad layer was removed.

Then this process was followed by two stages of polishing. The first stage used alumina paste having particles of (5µ) diameter, while the second stage was employed by the use of (0.5 µ) diameter of alumina paste in order to obtain good polished surface .The specimen was then cleaned with acetone to remove any dirt or greases.

In order to study the effects of heat treatment on pitting corrosion of this alloys (7020) the pitting corrosion experiments were carry out in3.5%NaCl with PH equal to (*5.4*).

linear polarization method used to determine both E_b and $E_{pitting}$ by applying constant potentials then recording current density .

The constant potential applied by the poteniostat by using the potentiostat (Tacussel type10-0.5). The reference electrode was Saturated Calomel Electrode (SCE)(Tacussel type Cu).The auxiliary electrode was platinum type (Tacussel type pt D10). The specimen of 7020 Al-alloy is working electrode.

The change in current density when using the preselected potential was applied, recorded automatically with time using and the current density versus voltage curve is plotted. The tests were performed by using a WENKING MLab multi channels and SCI-Mlab corrosion measuring system from Bank Electronics- Intelligent controls GmbH, Germany 2007. I_{PIT} and E_{PIT} were determined.

Microstructures of aluminum alloys 7020 were examined by Nikon ME-600 optical microscope provided with a NIKON camera, DXM-1200F.

Results and Discussion

Effect of Heating Temperature

Figs. (3-7) Show the effect of heating temperature at 1 hr holding time on the electrochemical behavior of 7020 AL-alloys in 3.5% NaCl. Solution. They indicate that increasing in heating temperature (100, 150,200,250,300,400,450,500) °C led to ◌̊ decrease in passive region of the alloy and shift the E b to more negative direction (-857.5, -828.7, -841.7, -916.2, &-939.2)Mv respectively(as shown in figs 5&,7).. From theses figures it can be concluded that, the pitting resistance of 7020 Al-alloys decreases with increasing heating temperatures (fig.3).

The microstructure of an alloy consists of solid solution and inters metallic particles (IMCs) remains un-dissolved, when heating at low temperatures(13, 14).

Inter metallic particles can be grouped into coarse inter metallic particles and fine precipitates in AL- alloys (10,11) . Coarse inter metallic particles. Form during the solidification process, while fine precipitates including hardening precipitates in the matrix and grain boundary precipitates form during aging process. (9,13).

As mentioned earlier (3,6,7) inter metallic particles play a critical role in localized corrosion of Al-alloys. The coarse inter metallic particles can be divided into two groups. Active particles and Noble particles relative to the Al-matrix. Therefore the inter metallic exhibit different electrochemical.

Properties from the Matrix. Mg containing phases are active to the matrix and act as anode(11). They are susceptible to active dissolution or (Mg) de-alloying when exposed in chloride solution(14).

However the higher level of precipitation hardening which occurs at high heating temperatures is the higher susceptibility to corrosion. Active components of the matrix alloy and the inter metallic phases may corrode selectively, resulting in changed corrosion properties.

Pitting is a highly localized type of corrosion in the aggressive chloride ions. Pits are initiated at weak sites in the oxide film by chloride attack. Pits propagate according to the following anodic reactions(2,5,7):-

$Al \longrightarrow Al^{+3} + 3e$ ………………………….. (1)

$Al(OH)_3 + 3H^+$ ………...(2) $\longrightarrow Al^{+3} + 3H_2O$

While hydrogen evolution and oxygen reduction are the important reduction processes at the inter metallic cathodes as(15):

$2H^+ + 2e \longrightarrow H_2$ ………………………….. (3)

$O_2 + H_2O + 4e \longrightarrow 4OH^-$ ………………… (4)

According reaction (2) the pH will decrease as pit propagate, therefore, the environment inside the pit (anode) changes to balance the positive charge produced by reaction 1and 2 chloride ions will migrate into the pit. The resulting HCl formation inside the pit causes accelerated pit propagation.

It is postulated that at the critical pitting potential breakdown occurs by a process of field assisted (Cl) adsorption on the hydrated oxide surface and formation of a soluble basic chloride salt which readily goes in solution. This salt was considered to be Alcl3 or Al(OH)2Cl.

The pitting current density as shown from these figures(3-8) and table (2) decreases sharply when the oxide film of Al2O3 give good protection against environment attack. The pitting current density have 9.9 A/cm2 when the alloys 7020 have heated ◌ً to 100 °C and remain 1hr then slow cooling in furnaces. This value indicates to low pitting corrosion and the oxide Al_2O_3 can be used as a protective film.

When the heating temperatures increases the current density of pitting corrosion increase this means that oxide film fail to protect the surface alloy from corrosion attack. From figures (3-7) the most value of current pitting corrosion take place at heating temperatures as follows:- 150> 400> 250> 300> 450> 500> 100 these results are attributed to the change only in the oxide film nature but also in the characteristics of the inter metallic particles and Al- matrix(15).

Effect of Holding Time

Figs.(3-7) show the effect of holding time on the electrochemical behavior of 7020 Al- alloys in 3.5% NaCl at various heating temperature (100, 150, 200, 250, 300, 350, 400, 450 and 500) °C. Figs (5.6&7) indicate that increasing holding time from one hour to two hours leads to increase the potential of pitting corrosion E_{pit} to more negative direction. This indicates that , the pitting resistance of 7020 Al-alloys decrease with increasing holding time of heating treatment.

The kinetics of phase precipitation are usually affected by the variations in holding time of heating temperature(16). This behavior can be attributed to the different in the micro- structure of the alloy. It had been observed that when holding time of heating temperature increase, the precipitation process would have sufficient time to occur. In work (17) had reported that time and temperature of heat treatment must be chosen to give the proper precipitate size, if temperature is too low, the critical dispersion is never achieved, although the hardness grows with time as the precipitate size increases. If the temperature is too high, the precipitated phases are too coarse. In this way, the system's free energy is lowered in steps, by passing through a series of metastable state on the road to equilibrium. Differ with the composition of the alloy, the first step, in the precipitation is the segregation of alloy element atoms into (Clusters) or platelets with a few any storms in thickness and a hundred angstroms in diameter, but still part of parent lattice. These platelets are often called Gainure- Preston Zones or GP1 Zones. In the next step the alloy element atoms diffuse to the GP1 Zone to form a larger one called DP2 Zone. At still stage a new transition phase which is coherent with the matrix, is precipitated and with increasing time and temperature of heat treatment, the coherent transition phases convert into the equilibrium precipitate without coherency.

The tendency to pitting corrosion is associated with these intermediate forms of precipitate (1.15).

In work (18) had been observed that optimum strength was obtained by treatment at 165°C for ten hours, after which , if the treatment time is prolonged rapid precipitation of non coherent particles would take place. In some time, the solid solution (Matrix) rejected the non- coherent phase. This process of detritions in structure due to faulty heat treatment is generally termed "reversion".

of; Ecorr , Icorr , Erp , and Eb estimated from tafel and cyclic polarization curves o Al 7020 at different heat treating Temperatures at {0ne &two hours} holding times.

Specimens Al 7020	**Heat treating temperature C°**	**E_{corr} / mv vs SCE**	**I_{corr} / μA/cm^2**	**Erp / mv vs SCE**	**Eb / mv vs SCE**
1	**With out(R.T.)**	**-745**	**14.3**	**-306**	**55**
2	**100/1h**	**-830**	**50.1**	**-305**	**48**
3	**100/2h**	**-870**	**53.5**	**-300**	**55**
4	**150/1h**	**-805**	**42.7**	**-330**	**50**
5	**150/2h**	**-819**	**47.0**	**-338**	**53**
6	**200/1h**	**-790**	**22.5**	**-350**	**0**
7	**200/2h**	**-822**	**25.9**	**-367**	**11**
8	**250/1h**	**-760**	**15.5**	**-358**	**14**
9	**250/2h**	**-810**	**18.6**	**-364**	**16**
10	**300/1h**	**-595**	**31.9**	**-197**	**23**
11	**300/2h**	**-630**	**33.8**	**-207**	**26**
12	**350/1h**	**-621**	**22.2**	**-211**	**24**
13	**350/2h**	**-609**	**17.9**	**-246**	**28**
14	**400/1h**	**-705**	**24.3**	**-198**	**82**
15	**400/2h**	**-700**	**19.9**	**-200**	**89**
16	**450/1h**	**-695**	**18.1**	**-166**	**110**
17	**450/2h**	**-691**	**15.8**	**-176**	**118**
18	**500/1h**	**-680**	**12.4**	**-198**	**145**
19	**500/2h**	**-663**	**11.6**	**-220**	**153**

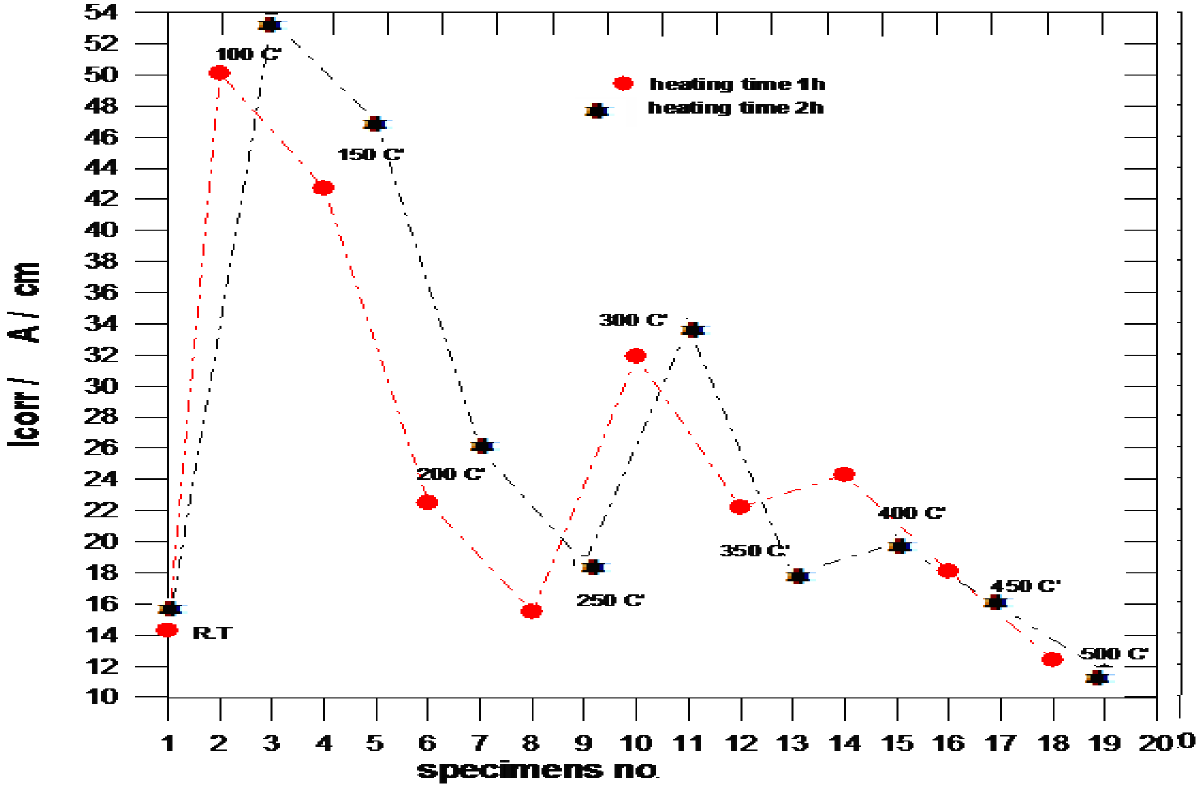


Figure (3) Icorr of different specimen's conditions as listed in table (2)

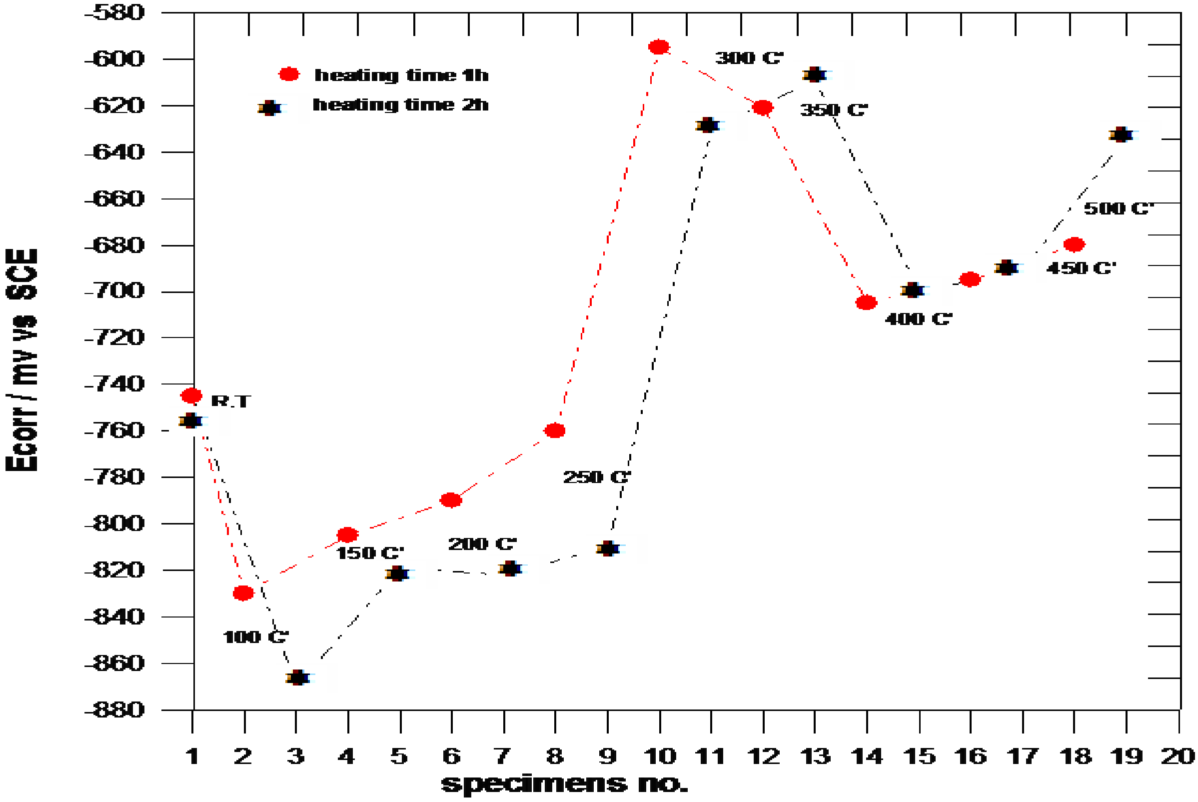


Figure (4) E corr at different specimen's conditions as listed in table (2)

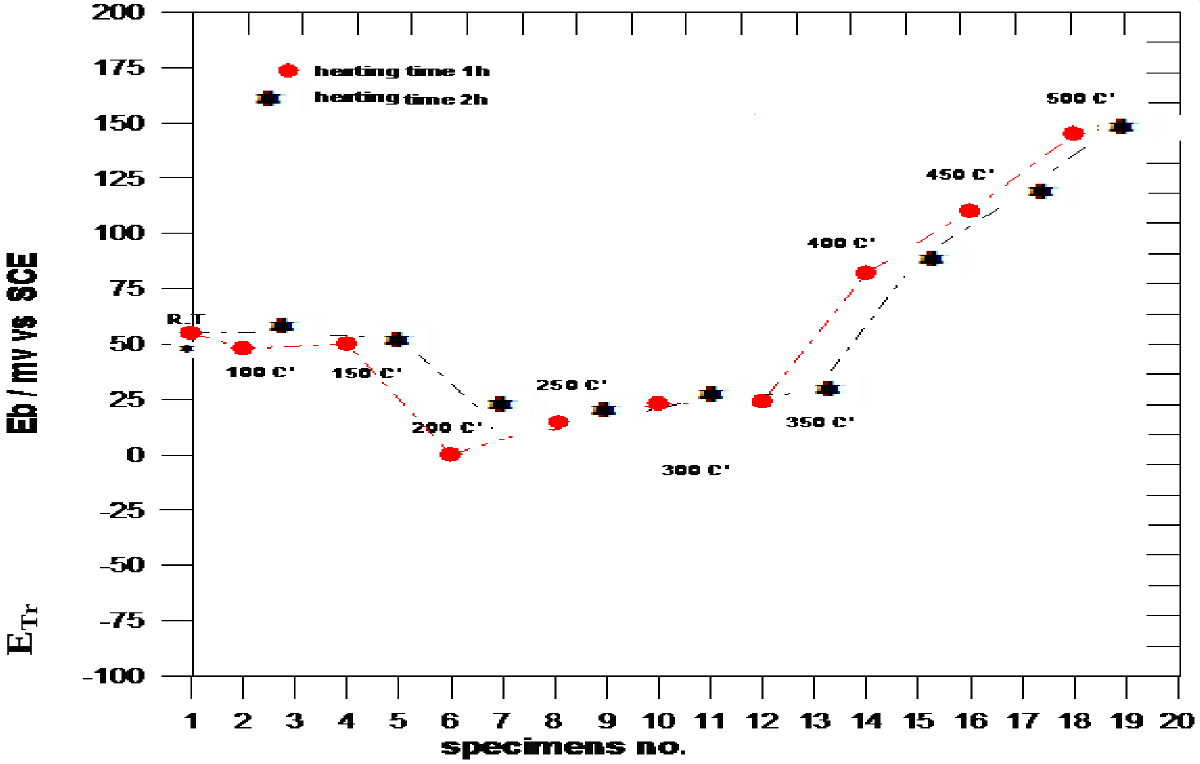


Figure (5) Eb at different specimen's conditions as listed in table (2)

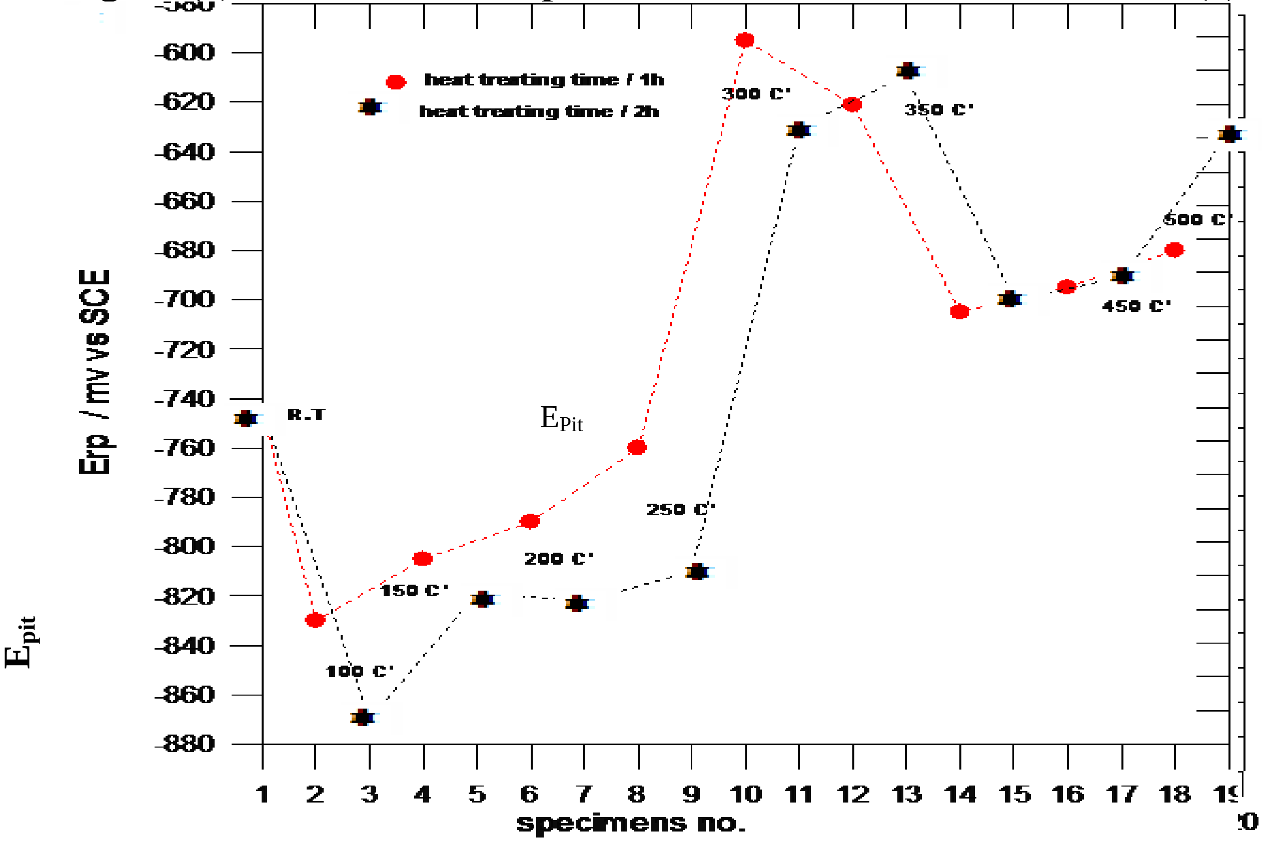


Figure (6) Erp at different specimen's conditions as listed in table (2)

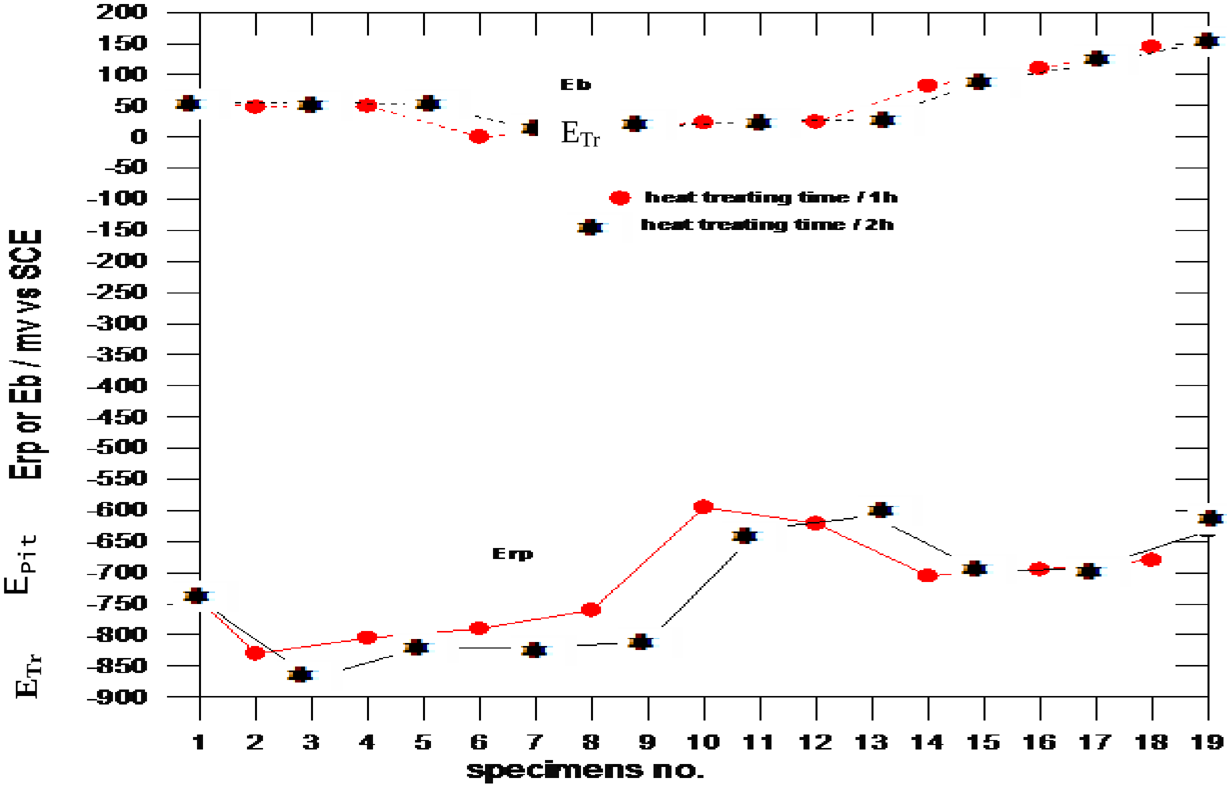


Figure (7) E $_{rp}$ & Eb at different specimen's conditions as listed in table (2)

Conclusions

1- Corrosion resistance of 7020 Al-alloy has significant by heat – treatment of the alloys.

2- As temperatures of heat treatment increase from 100-500°C pitting corrosion appears on the precipitated phases.

3- Pitting corrosion tendency increase with increastemperature of heating.

4- Increase time holding of heat treatment from 1 hr. to 2 hrs would increase the pitting corrosion.

5- The pits shape is a function of intermetallic particles shape.

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الخلاصة:

تمت دراسة تاثير متغيرات المعاملة الحرارية (درجة الحرارة والزمن) على سبائك المنيوم عالية المقاومة من نوع ٧٠٢٠ .

اجريت التجارب بواسطة تسخين العينات في درجات حرارة مختلفة (١٠٠ ، ١٥٠ ، ٢٠٠، ٢٥٠ ، ٣٠٠ ، ٣٥٠ ، ٤٠٠ ، ٤٥٠ ، ٥٠٠) م° . ضمن زمن فترة ساعة وساعتين .

اثبتت نتائج البحث ان. :

- المعاملات الحرارية لها دور مهم على مقاومة التآكل لسبيكة الالمينوم Al-7020.
- كلما زادت درجة الحراة للمعاملات الحرارية من (١٠٠–٥٠٠)°م كلما زاد ظهور التآكل النقري على الاطوار المترسبة .
- شدة التآكل النقري يزداد مع زيادة درجة الحرارة .
- زيادة الزمن للمعاملة الحرارة من (١–٢) ساعة يؤدي الى زيادة التآكل النقري .