

THE DEPENDENCE OF PITTING CORROSION MORPHOLOGY ON THE PRECIPITATED PHASES FOR 7020 AL-ALLOY

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Abstract

Al-alloy type 7020 was heated at different temperature (from 100 to 500) °C to observe the shape of precipitated phases. Pitting corrosion of this alloy was also studied by using immersion in 3.5% NaCl and polarization techniques. The aim of this paper is to find the dependence of pitting corrosion morphology on the precipitated phases for 7020 Al-alloy.

The results are confirmed that, at low heating temperatures between (100-200) °C dendrite structures were observed. These zones suffered dendrite pitting corrosion, when the alloy was exposed to corrosive medium of 3.5% NaCl. At the intermediate temperatures range (250-350) °C, different shapes precipitated phases are obtained. As heating temperature was increased these shapes converted from dendrite to spherical shapes. This transition in shapes was also observed for developed pit. At heating temperature up to 500 °C most of the formed pitting has the spherical overall shapes corresponded with the phases shape, precipitated at these range of temperatures.

اعتمادية التكوين التشكيلي (مورفولوجيا) للتآكل النقري على الاطوار المترسبة
7020 في سبيكة المنيوم نوع

الخلاصة

سخنت سبيكة المنيوم من نوع 7020 بدرجات حرارة مختلفة تقع ما بين (100-500)°م لغرض معرفة شكل الاطوار الثانوية المترسبة. وفي نفس الوقت تمت دراسة التآكل النقري لهذه السبيكة بطريقتين : الغمر في محلول 3.5% كلوريد الصوديوم وطريقة الاستقطاب. يهدف البحث الحالي الى ايجاد اعتمادية التكوين التشكيلي (مورفولوجيا) للتآكل النقري على الاطوار المترسبة في سبيكة المنيوم نوع 7020. اكدت نتائج البحث ان تسخين هذه السبيكة عند درجات حرارة منخفضة (100-200) °م اعطت بنية مجهرية شجرية الشكل . ان هذه المناطق الشجرية المتكونة هي التي تآكلت عند تعرض السبيكة الى محلول اكل من 3.5% كلوريد الصوديوم. اما تسخين السبيكة الى درجات حرارة متوسطة واقعة ما بين (250-350) °م فقد اعطت بنية مجهرية ذات اشكال مختلفة. كلما ارتفعت درجات الحرارة يتحول شكل الاطوار المترسبة في البنية المجهرية من الشكل الشجري الى شكل قريب الى الشكل الكروي. ان التحول في الاشكال لوحظ ايضا في شكل التفرعات بحيث عندما تصل درجة حرارة التسخين الى اكثر من 500 °م ستمتلك اغلب التفرعات الناتجة من التآكل الشكل الكروي والذي يتطابق مع شكل الاطوار المترسبة عند هذه الدرجات الحرارية.

Introduction

Pitting corrosion is the localized corrosion of a metal surface confined to a point or small area ⁽¹⁾, which appears as holes or pits on the metal surface. Pit shapes can be simply divided into isotropic and anisotropic groups. Shapes are isotropic, if are isotropic and are called micro structural orientated pitting, which may be producing due to intergranular corrosion ⁽²⁾

The variation in pit shape could mainly depend on the microstructure of metals or alloys such as alloy composition and aspect ratio of grains ⁽³⁾. Pitting corrosion forms on passive metals and alloys can become elliptical, subsurface, undercutting, horizontal, vertical, wide, shallow, narrow and deep. The shape of pitting can only be identified through metallographic, where a pitted sample is cross sectioned and the shape, the size and the depth of penetration can be determined. Pit nucleation and propagation are related to precipitated phases on the grain boundaries. Precipitates form by nucleation and growth from a supersaturated solid solution during natural or low temperatures artificial aging.

The precipitation is the segregation of alloy element atoms into (Clusters) or platelets with a few angstroms in thickness and a hundred angstroms in diameter, but still part of parent lattice. These platelets are often called Guinier- Preston Zones or (G.P) zones. These precipitates can be spherical, needles laths, plate among other shapes. When they are homogeneously dispersed their effect on localized corrosion behavior is difficult to dissolve, however, when they are concentrated on grain boundaries, they may affect intergranular corrosion ⁽²⁾. The initial precipitation usually occurs along grain boundaries or slip planes and hence the depleted solid solution zones will first develop along these boundaries. Depleted zones, being the most anodic, corrode selectively by an electrochemical process, producing pits or crevices. Pit morphology plays an important role in the transition to stable pitting and thus the pitting potential. Pit propagation and orientation faceted corrosion pits are widely observed and may be more common than smooth hemispherical pits. Faceted pits were probably first observed in dislocation etch pit experiments. While there is ample evidence in the literature to demonstrate that dislocations may be used to produce pits in metal surfaces at the location where a dislocation penetrates the free surface ⁽⁴⁾, there is no relationship between the movement of the dislocation (or dislocation pile-up) through the lattice and pit geometry. The most common explanation for preferentially

oriented pits / propagation is surface energy. Surface energy is a fairly general term to describe dangling bonds at a free surface - more closely packed surfaces often having lower surface energy as they loose the fewest number of bonds per unit area when the new surface is formed⁽⁵⁾. However, this simple "hard-sphere" model of the surface does not adequately describe the lattice and does not predict the observed trends in pitting potential or pit morphology in some systems. This does not mean that bonding as a model is incorrect, rather, that our concept of surface energy needs to be modified. Sufficient area of susceptible low index planes may be the necessary criterion for pit stability where crystallographic pitting is observed⁽⁵⁾.

Pitting corrosion has been studied for many year ago⁽⁶⁻⁹⁾ but their morphology is less well understood. Information is still required to explain the dependence of pitting corrosion morphology on the precipitated phases. This paper is an attempt to attribute the different shapes and pit morphology to the microstructure changes of the 7020 Al-alloy after heating at different temperatures.

Experimental Work

A plate of aluminum alloys (7020) having dimension (300 x 80) mm with a thickness of 10mm are received from the local market . The chemical composition of the received alloys compared with standard condition of 7020 AL- alloys are shown in table (1). The chemical composition analysis was carried out by using spectrometer in the Institute of Specialized Engineering.

Specimens of (25x30) mm were cut from the metal plate .The surface to be tested have (25x25) mm; upper edge (5) mm was left. In order to hang the specimen in the solution from (2) mm diameter hole which located in the center upper edge of (5) mm. Heat treatment achieved in production engineering and metallurgy department / university of technology by using electrical furnace type GARBOLITE – SHEFFIELD-ENGLAND +15°C with maximum of 1200°C. Heat treatment was done by homogenization treatment at 100150,200,250,300, 350, 400, 450 and 500 °C, for 1hr & 2hrs and cooled in furnace.

The pitting corrosion experiments were carrying out in sodium chloride (NaCl) solution with (3.5) wt% concentrations and pH equal to (5.4). Specimens are insulated & isolated electrically from contact with another metal to avoid any galvanic effects. All original area of (25 x 25) mm is completed immersion in the tested solution 3.5%NaCl 3.5%NaCl in demonized distilled water.

The corroded metal surface is visually examination while, the corrosion products are analyzed in the material department in the science and technology ministry by using x-ray diffraction unit model XRO – 6000 , kv = 40 , Cu K type Twin x , (EDXRF). The corroded metal surface is also examined microscopically. Microstructures of aluminum alloys 7020 were examined by Nikon ME-600 optical microscope provided with a NIKON camera, DXM-1200F.

Linear polarization method used to determine both $E_{corr.}$ and $I_{corr.}$ by applying constant potentials then recording current density. The polarization cell (Figure 2), consists of a cylindrical glass reaction vessel with 3 liters capacity, lugging capillary probe, reference electrode and a thermometer. All potentials were measured with a reference to saturated calomel electrode (SCE).

Potentiostat type Wenking LT 87 in the science and technology ministry is used, in which cyclic polarization curves were automatically recorded. The polarization apparatus used in this work is shown in figure (1) .It consists mainly of:

Potentiostat (Wenking LT. 87), Polarization cell, Rotating cylinder electrode assembly, Digital multimeters and Constant temperature bath (Memert P21S6).

Results and Discussion.

Pitting is influenced by the intermetallic particles which exhibit different characteristics to the matrix and may be either anodic or cathodic relative to the matrix. From localized corrosion perspective, the dominate feature of alloy microstructures is the distribution of second phase {intermetallic} particles ⁽⁶⁾. The range of corrosion potentials observed for the different intermetallic varies over several hundreds of mill volts, reflecting the electrochemical heterogeneity that may be found in many commercially Al-alloys.

The nucleation sites of pit are frequently found to be related to the microstructure of the alloy. Their location is usually found to be associated with intermetallic phases. Intermetalliac phases act as initiation sites for localized corrosion. It is clear that, pit formed at the site of phases, and corrosive attack on phases was more severe ⁽¹⁰⁾. Pits have the shape of the active phase, which may corrode preferentially. It will be observed that precipitation occurs more rapidly at the grain boundaries than within the grain the boundaries becoming anodic to the grain centers .

At low heating temperatures between (100-200) °C dendrite structures were observed. In this condition dendrite pitting attack is promoted and the coherent

precipitates are the most desirable for pitting corrosion. This is particularly remarkable for the shape of precipitates as shown in figure (2). Heating at low temperatures results in a fine distribution of (G-P) zones, therefore these zones suffered pitting corrosion. The pit growth usually takes also fine distribution of shapes. Commonly such particles will exhibit electrochemical characteristics that differ from the behavior of the matrix, rendering the alloy susceptible to localized forms of corrosion.

At the intermediate temperatures range (250-350) °C transition structures between the dendrite and sphere morphologies are observed. As heating temperature increases (G.P) zones grow into indirect phases of (Mg_xZn_y) or $(Al_2Mg_3Zn_3)$ ^(6,7), therefore the alloy hardness increasing with increasing temperature. During heating at elevated temperatures (250-350)°C, precipitation of discrete particles occurs, with more advanced precipitation at the grain boundaries than in the grain matrix. The grain boundaries are surrounded by narrow zones of precipitated phase's that etch smoothly. These zones become more active and will corrode in 3.5% NaCl as potential increases. Moreover, pit nucleation and propagation occur in the zones where $MgZn_2$ is accumulated which take place at heating temperature 250 – 350 °C. Pits have the shape of the active phase, which may corrode preferentially.

These phases may serve as critical anode and provide cathodic protection to the surrounding matrix ⁽⁶⁾. At these heating temperatures, dark portions have been formed as shown in figure (2). The portions consist of a mixture of α -Al and precipitates. The micro galvanic effects between the matrix and the intermetallic particles is generally believed to result in pitting corrosion as shown in figure (2). Pitting corrosion is a result of galvanic corrosion between anodic grain- boundary precipitates and the depleted zones, rather than between the matrix and the depleted zone. Figure (2) shows the change in morphology of the grain boundaries and pit morphology with the duration of heating at 250- 350 °C.

It can be seen from the figure (3), that with increasing heat treatment temperature (up to 500°C), the corrosion resistance decreases. This is an important case related to a mount of precipitated phases. These results support the observations in figures (3&4), which shows the values of **E_{corr}** and **I_{corr}** estimated from cyclic polarization curves for 7020 Al - alloy at different heat treating temperatures and at constant holding times. However, the higher level of precipitation is the higher susceptibility to corrosion.

Tables (3&4) show the Analysis of x – ray diffraction analysis of Al alloy 7020 at 400⁰C before and after immersion respectively. These results refer that, the degree of both precipitation and corrosion susceptibility is a function of heated temperature and holding time.

At heating temperature 400 °C a transition from the dendrite to the spherical structure was observed. Most of the phases have the spherical overall morphology as indicated in the figure (2), but there are occasional regions, where the phases have a more elliptical or elongated morphology and these regions are invariably closely associated with the primary dendrites as shown in figure (2).

At high temperature the dendrite morphology disappeared and spherical crystals were formed. The phase has the general spherical overall shape with a distinctly lamellar internal structure.

These results give good evidence that the heat treatment temperature and holding time have an important and same effect on both microstructure of alloy and their electrochemical properties. However, the higher level of precipitation is the higher susceptibility to corrosion. As the heating temperature increased, the pit became deeper due to the high precipitation of the phases. And also to the dissolution of these precipitations. Pits of this type are often deep and may have remnants of the particle in them. This morphology has been interpreted as particle fall- out, selective particle dissolution in case of electrochemically active particles.

However, pitting morphology can vary depending upon intermetallic morphology for 7020 Al-alloys. These results showed a good agreement with the results obtained in work. (7, 10)

Conclusions

- 1- The heat treatment temperature and holding time have an important and same affect on both microstructures of 7020 Al-alloy and their electrochemical properties.
- 2- As increasing heat treatment temperature (up to 500°C), the corrosion resistance of 7020 Al-alloy decreases.
- 3- At low heating temperatures between (100-200) °C dendrite structures were observed and the coherent precipitates are the most desirable for pitting corrosion. In this condition dendrite pitting were observed.

4- At the intermediate temperatures range (250-350) °C transition structures between the dendrite and sphere morphologies are observed which corresponding with the shape of pits, resulting when the specimens were exposure to 3.5% NaCl.

5- At high heating temperature over 400 °C, the dendrite shape Most of the phases have the spherical overall morphology disappeared and spherical crystals were formed and most of the formed pits have the spherical overall shape.

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Table (1) The chemical composition of 7020 Al- 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

Table (2) Dissolution potentials of intermetallic phases
(solution NaCl, H₂O₂ ASTM G 69)

solid solution	Dissolution potential (m V SCE)	Intermetallic phase
Al-5Zn	- 970	
	- 1150	Al₃Mg₂
	- 1190	Mg₂Si
Al-1Zn	- 850	
	- 910	Al₂CuMg
	- 960	MgZn₂
Al-3Mg	- 780	
Al-5Mg	- 790	
	- 430	Al₃Ni
	- 470	Al₃Fe
Al-4Cu	- 610	
	- 640	Al₂Cu
Al-1Mn	- 650	
	- 760	Al₆Mn

Table (3) Analysis of x – ray diffraction at 400°C before immersion.

Sample	Temperature	2 θ	D(A ⁰) measured	D(A ⁰) standard	Phases
B	100	40.5	2.225	2.23	MgZn
		41.4	2.179	2.182	MgZn ₂
		45.4	2.330		Al
		38.6	2.02	0.02	Al
		44.8			
		37.2	2.41	2.40	Al ₃ Mg ₂
B	450	45.0807	2.009	2.02	Al

		40.55	2.222	2.22	Mg ₄ Zn ₇
		38.06	2.362	2.36	MgZn
		41.5	2.174	2.18	MgZn ₂
		42.01	2.251	2.25	MgZn ₂
		44.85	2.018	2.01	MgZn ₂
C	400	41	2.199	2.182	MgZn ₂
		44.5	2.03	2.02	Al
		40.5	2.225	2.22	Mg ₄ Zn ₇
D	350				

Table (4) x – ray diffraction analysis of 7020 at 400⁰C after immersion

	2θ	D(A)	D(A) standard	Phases
400 °C	38.8	2.319	2.30	MgZn
1 hr.	40.44	2.179	2.182	
	45	2.01	2.02	Mg ₄ Zn ₇
	42.4	2.130	2.16	Al
				MgZn ₂
400 °C	40.6	2.220	2.22	Mg ₄ Zn ₇
2 hr.	38.45	2.319	2.30	MgZn
	45	2.01	2.02	Al

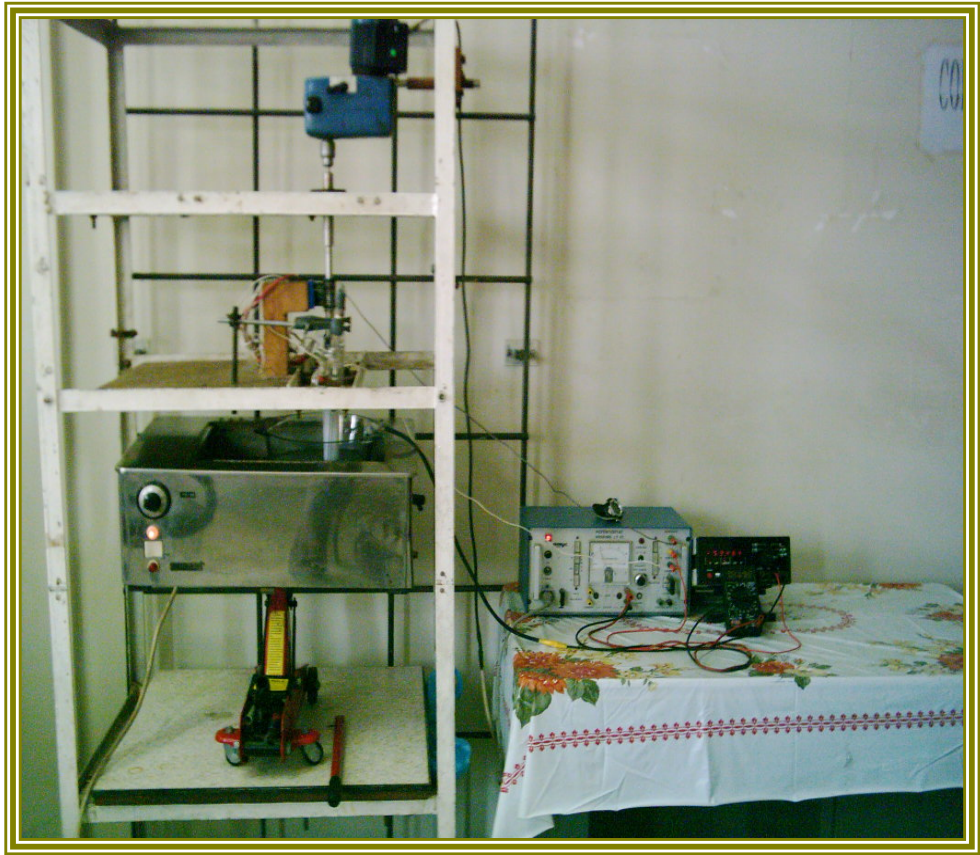
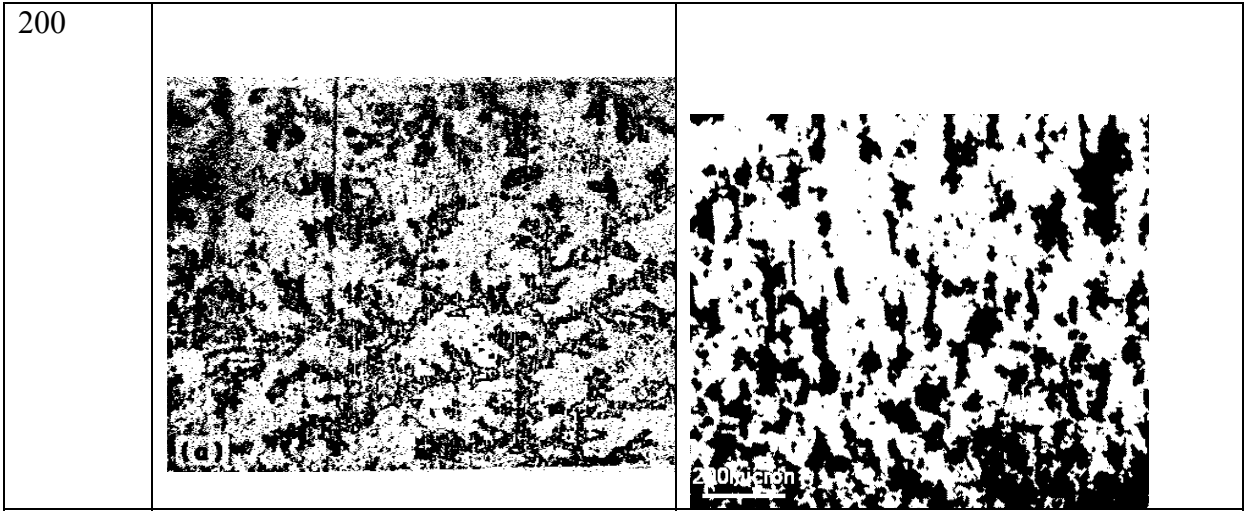
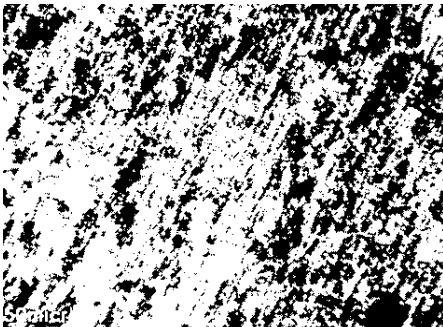
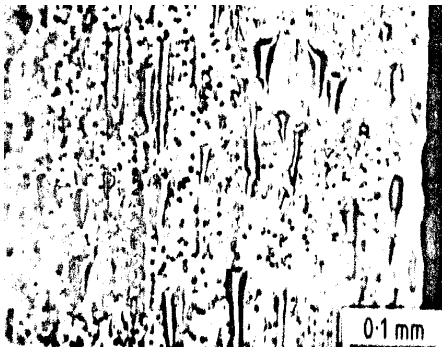
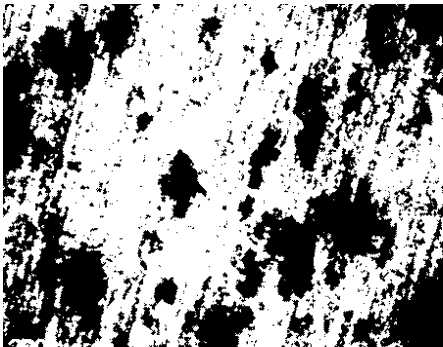
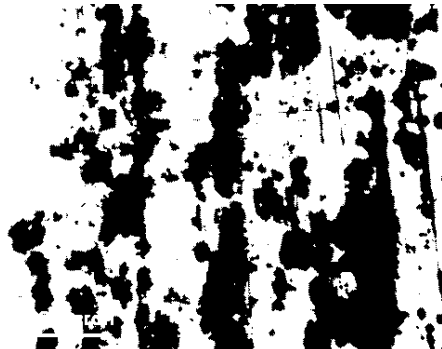
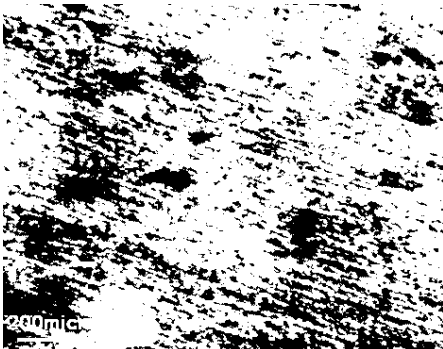
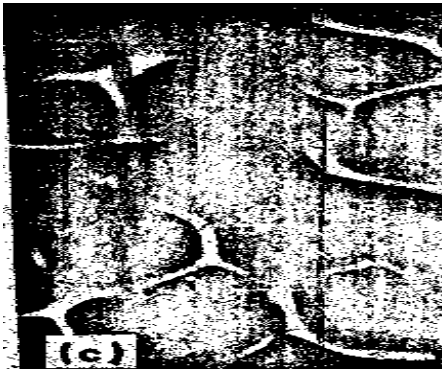


Fig.(1), polarization apparatus of corrosion test.

A

B



250		
300		
350		
400		

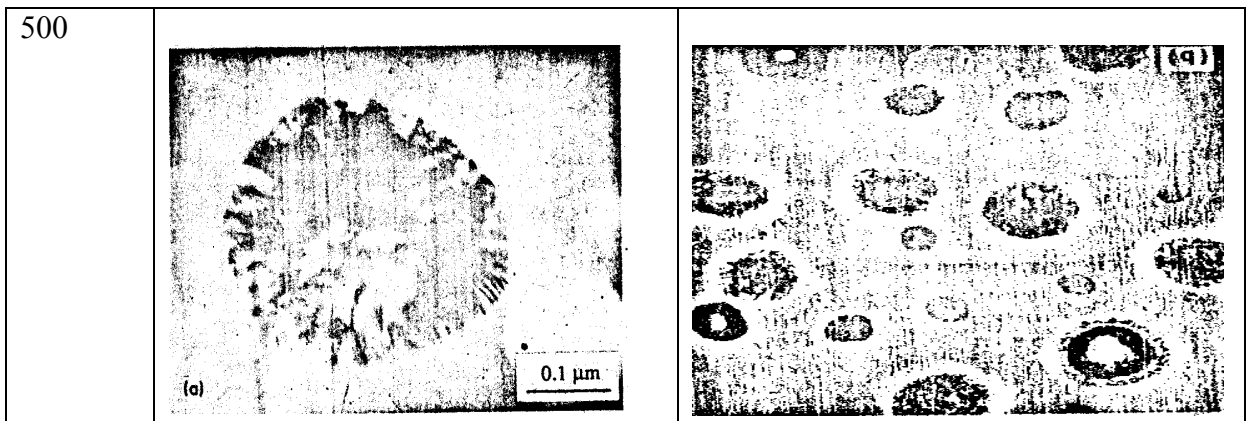


Fig. (2). Comparison Pit shape (A) with the predicated particles shape at different heating temperatures for two hours holding Time (B).

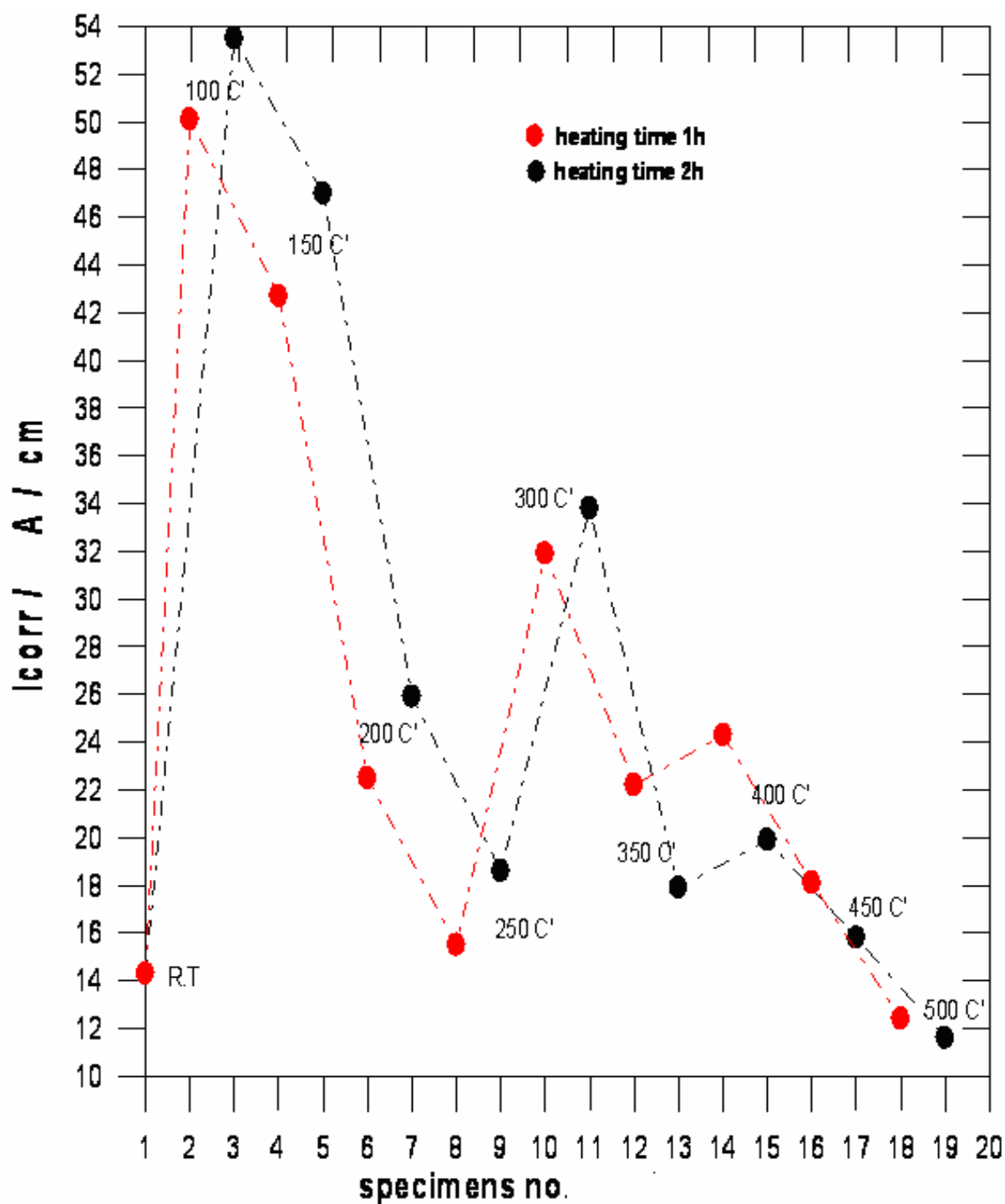


Fig.(3) I_{corr} . at different specimen's conditions

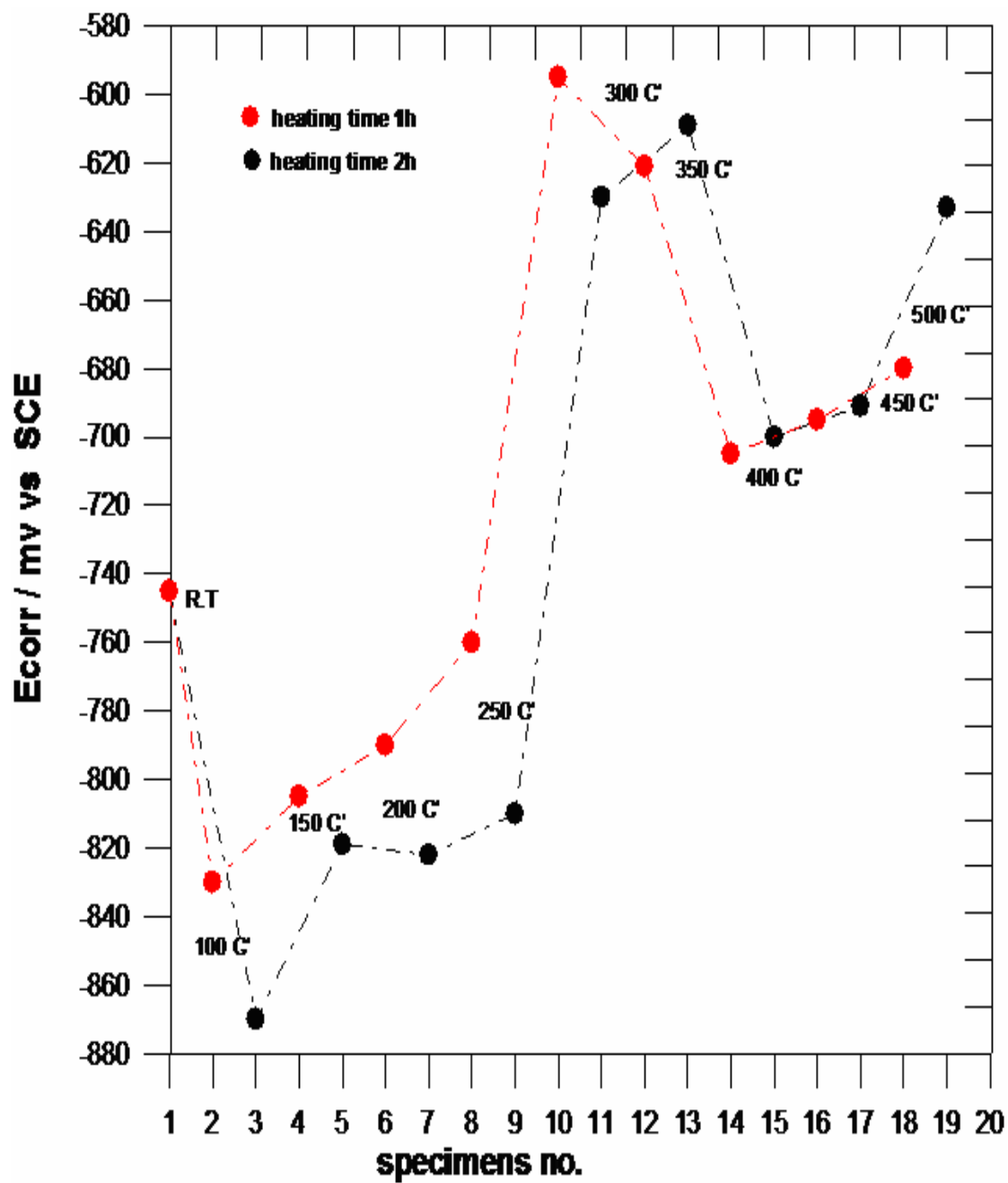


Fig. (4) E_{corr} . at different specimen's conditions .