

Corrosion, Passivity and Pitting of Inconel (600) in Sulphuric Acid

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Abstract

A potentiostatic study of the behaviour of Inconel (600) in molar sulphuric acid has been carried out over the temperature range 293-313 K. Values have been established for the potentials and current densities of the corrosion, active-passive transition, passivity and transpassive states. For corrosion, the current density (i_c) and potential (E_c) have been determined from well-defined Tafel lines. The potential and current density prior to the commencement of passivity have been obtained corresponding respectively to the critical potential (E_{cr}) and to the current density (i_{cr}) for the active-passive transition state. The passive range was defined by the respective potentials and current densities for passive film formation and dissolution. The dissolution point was correlated with transpassive potential (E_t) and current density (i_t). All the estimated potentials and current densities for the various states were influenced by temperature and the presence of additives in the sulphuric acid. Additives such as nitric acid, thiourea and sodium chloride lowered the corrosion current density (i_c) of the alloy while hydrochloric acid enhanced the value of i_c . Addition of thiourea or sodium chloride or hydrochloric acid caused a shift in the corrosion potential (E_c) to less negative values while nitric acid shifted E_c to more negative potentials. The kinetic effect of the additives have been studied. Values of activation energy (E) were considered to be apparent and some negative values of E have been obtained with certain additives for the critical and passivity processes. Such negative E values were attributed to small values of true energies of activation together with relatively large exothermic enthalpies of such processes.

Key words: potentiostatic study, polarization curve, Critical State, Passivity State, Transpassive State.

Introduction

Nickel is important as an alloy addition and as a base material for corrosion resistant alloys [1]. Studies have demonstrated the usefulness of potentiostatic polarization techniques for

characterizing active-passive transition and predicting the corrosion behaviour. Here, these techniques are utilized to study the active-passive characteristics of an important alloy of nickel, Inconel

(600), in which nickel is present as a base-alloying metal.

Inconel (600) possess a high degree of resistance to corrosion when exposed to atmosphere or to fresh and natural water, and the alloy exhibits little tendency to breakdown even in acidic solution containing NaCl [2]. Because of the high resistance of this alloy to corrosion in high purity water, it is used quite frequently in nuclear reactors for steam generator tubing and water piping [3].

The present paper was designed to cover the full potentiostatic polarization behaviour of Inconel (600) in sulphuric acid solution in the absence and the presence of certain other substances which are known for their inhibiting or passivity or depassivating properties in such medium. The research covered the Tafel regions of the polarization curve and the active-passive transition region which is described as the critical region. The work also covered the passivity range and the subsequent transpassive behaviour where pitting of the alloy may become possible. The influence of nitric acid, thiourea, sodium chloride and hydrochloric acid on the various polarization regions has been extensively investigated. No such work has so far been reported in the literature.

Material and Methods:

The Inconel (600) specimen had the following composition as revealed by emission spectroscopic analysis

Table (1): Composition of Inconel (600) alloy.

Element	Ni	Cr	Fe	C	Mn	Si
wt %	76.0	15.5	8.00	0.08	0.50	0.25

Analar grade chemicals have been used for the preparation of the solutions.

Circular working electrode with 1cm² surface area have been used, the test specimen was polished with emery paper in different grades (320, 500, 1000, 2400, 4000), then washed with

acetone and finally rinsed with distilled water.

The electrolytic cell had a working capacity of 750 cm³ which contained the working electrode, platinum auxiliary electrode and saturated calomel reference electrode. The latter was brought close to the

working electrode through a Luggin capillary bridge which was filled with the test solution. The temperature of the cell solution was adjusted electrically to ± 0.01 °C.

The potential-current polarization curves were plotted using a potentiostat (WENKING M Lab multichannel and SCI-M Lab corrosion measuring system from Bank Electronics- Intelligent controls GmbH, Germany 2007). This instrument was interfaced to an external computer via the RS 322 interface, M lab is controlled from M Lab Sci computer software using Window XP. The M lab software cares for control of the potentiostats, recording of data and also data processing. The potential of the working electrode started at -1.0V with a scan rate of 3mV.s⁻¹ until the potential became +1.4V versus a saturated calomel electrode.

Results and Discussion

The potentiostatic polarization curve, presented in Fig. (1), shows parts A, A', B, C, D and E. The section A'-A shows the cathodic process in which hydrogen ions are discharged which is followed by hydrogen gas evolution. The section A-B of the curve shows a remarkable increase of anodic dissolution current, corresponding to the active dissolution zone of the alloy. In the B-C-D section of the curve the anodic current sinks to a very low value, in compliance with an exponential law, maintaining itself at the diminished value over a wide potential range (0.10 to ~0.85V); this is the passivity range. The onset of passivity, corresponding to the formation of a

passive oxide layer on the alloy surface occurs at a definite potential, called the activation or Flade potential. The potential corresponding to point C on the polarization curve (Fig. (1)) represents the Flade potential. A point on the region C-D of the curve where the current density decreases to its lowest value describes the passive current density (i_{pas}) and the potential corresponding to this point is the passive potential (E_{pas}).

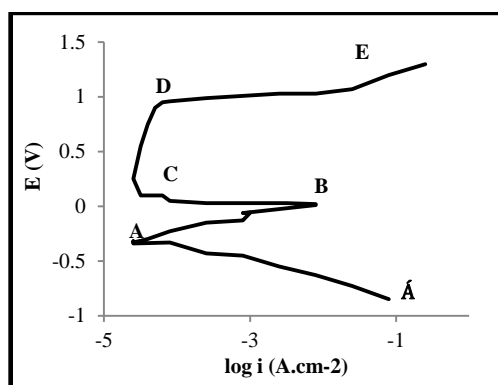


Fig. (1): A typical polarization curve for the corrosion of Inconel (600) in 1 mol.dm⁻³ of H₂SO₄ solution at 293 K.

In the potential-current curve of Fig. (1), the highest value of the anodic dissolution current before the alloy becomes passive (point B on the curve) represents the critical current density (i_{cr}). It makes an important change in the kinetics of the electrode reaction namely, the change from a high dissolution rate (active state) to a very low dissolution rate (passive state). As the voltage is increased, the current density increases substantially along the section D-E and corrosion resumes in the transpassive range. Beyond the point E on the curve (Fig. (1)), the alloy undergoes corrosion at a constant current density in a similar manner to the stage prior to passivation. The current density and the potential corresponding to the point E may represent the pitting current density (i_p)

and the pitting potential (E_p) respectively.

The potential and the current density corresponding to the point A (Fig. (1)) represent respectively the corrosion potential (E_c) and current density (i_c) of the alloy. Values of E_c and i_c are usually determined by extrapolating the linear logarithmic sections of the cathodic and anodic Tafel lines to the point of intersection. Table (2) presents the potentials and current densities corresponding to corrosion, critical (cr), passivity (pas) and pitting (p) states for Inconel (600) in 1M sulphuric acid in absence and the presence of certain substances which are known for their inhibiting action.

Addition of nitric acid at a concentration of 1.24×10^{-3} mol dm⁻³ to molar H₂SO₄ solution caused an initial change in the corrosion potential (E_c) to more negative values indicating an increasing corrosion tendency of the alloy in sulphuric acid. Further additions of nitric acid (Table (2)) resulted in the variation of E_c to less negative values. The corrosion current density (i_c) decreased with the first two additions of nitric acid (1.24×10^{-3} mol dm⁻³, 1.24×10^{-2} mol dm⁻³) which was followed thereafter with an increase in i_c . The inhibiting effect of nitric acid in the corrosion of Inconel (600) in molar H₂SO₄ solution is obvious in the lower i_c values than that when nitric acid was absent.

The lowering of i_c value than the 3.20×10^{-5} A.cm⁻² which was recorded for Inconel (600) in sulphuric acid was substantial by all thiourea additions reflecting the greater inhibiting effect of this substance as compared with other inhibitors (Nitric acid, Sodium chloride) of Table (2). The order of inhibiting follows the sequence:

Thiourea > Nitric acid > Sodium
chloride

Table (2): Corrosion potentials (E_c) and current densities, critical potentials (E_{cr}) and current densities (i_{cr}), passive potentials (E_{pas}) and current densities (i_p) for Inconel (600) in 1M H_2SO_4 solution at 293 K in the absence and presence of various concentrations (C) of certain inhibitors.

inhibitor	C (mol.dm ⁻³)	corrosion			Critical		Passive		Pitting	
		- E_c (V)	i_c (A.cm ⁻²)	P%	E_{cr} (V)	i_{cr} (A.cm ⁻²)	E_{pas} (V)	i_{pas} (A.cm ⁻²)	E_p (V)	i_p (A.cm ⁻²)
—	0	0.390	3.20×10^{-5}	-	- 0.070	4.44×10^{-4}	0.45	3.95×10^{-5}	0.900	5.00×10^{-5}
Nitric acid	1.24×10^{-3}	0.405	1.26×10^{-5}	60.63	- 0.072	8.00×10^{-3}	0.46	8.87×10^{-6}	0.900	0.24×10^{-5}
	1.24×10^{-2}	0.400	1.18×10^{-5}	63.13	- 0.075	8.75×10^{-3}	0.46	7.62×10^{-6}	0.900	0.87×10^{-5}
	1.23×10^{-1}	0.380	2.72×10^{-5}	15.00	- 0.085	3.50×10^{-3}	0.46	6.70×10^{-6}	0.900	1.40×10^{-5}
Thiourea	1.00×10^{-3}	0.330	0.32×10^{-5}	90.00	0.000	4.00×10^{-3}	0.52	0.25×10^{-4}	0.890	2.00×10^{-5}
	1.00×10^{-2}	0.320	0.25×10^{-5}	92.19	0.060	7.20×10^{-3}	0.54	1.25×10^{-4}	0.920	1.57×10^{-4}
	1.00×10^{-1}	0.370	0.87×10^{-5}	72.81	0.150	9.53×10^{-3}	0.56	1.25×10^{-3}	0.930	3.95×10^{-4}
Sodium chloride	1.25×10^{-3}	0.380	2.33×10^{-5}	27.19	- 0.080	3.25×10^{-3}	0.44	0.59×10^{-5}	0.890	0.14×10^{-4}
	1.25×10^{-2}	0.370	2.23×10^{-5}	30.31	- 0.070	6.55×10^{-3}	0.46	4.52×10^{-5}	0.890	1.25×10^{-4}
	1.25×10^{-1}	0.380	0.99×10^{-5}	69.06	- 0.060	1.25×10^{-2}	0.52	3.12×10^{-5}	0.890	0.63×10^{-4}
Hydrochloric acid	2.00×10^{-2}	0.360	4.75×10^{-5}	-	0.010	8.12×10^{-3}	0.52	0.87×10^{-5}	0.920	1.47×10^{-4}

The value of i_c with hydrochloric acid addition became greater than when this acid was absent in the sulphuric acid. This implies an accelerating effect of hydrochloric acid for the corrosion of Inconel (600) in sulphuric acid (Table (2)).

The values of the corrosion potential (E_c) were generally less negative in the presence of such substances as thiourea, sodium chloride and hydrochloric acid. The extent of change in E_c values towards less negative values followed the sequence:

Thiourea > Hydrochloric acid > Sodium chloride

On thermodynamic ground, a shift of E_c values toward less negative potentials reflects a decrease in the tendency of the alloy for corrosion [4].

The Critical State

This was described by the current density (i_{cr}) and potential (E_{cr}) corresponding to the point B on the polarization curve of Fig. (1). Values of

E_{cr} did not change significantly when nitric acid or sodium chloride (Table (2)) were present in the corrosion medium (sulphuric acid). A significant change in the sign and the magnitude of E_{cr} was observed when thiourea or hydrochloric acid was present in sulphuric acid. Thus, thiourea and hydrochloric acid caused a shift in E_{cr} to more noble potentials decreasing the tendency of the alloy to attain the critical state considerably.

The critical current density (i_{cr}), on the other hand, increased considerably by the addition of thiourea, nitric acid, hydrochloric acid and sodium chloride. The extent of increase in i_c values was higher in the case of thiourea and lower with sodium chloride.

The Passivity State

Neither the passivity range (C-D) nor the passive potential (E_{pass}) altered significantly in the presence of nitric acid, thiourea, sodium chloride and hydrochloric acid in sulphuric acid

solution. The change of E_{pas} value was somehow greater by the addition of thiourea and hydrochloric acid and the shift was towards more noble potentials (Table (2)).

The passive current density (i_{pas}) generally decreased when other substances were present in sulphuric acid (Table (2)) except for the higher thiourea concentrations (1×10^{-2} , 1×10^{-1}) mol.dm⁻³. The decrease in the value of i_{pas} was substantial when nitric or hydrochloric acid was present in the sulphuric acid. The extent of decrease in i_{pas} of Inconel (600) in molar sulphuric acid by the influence of additives followed the sequence:

Nitric acid > Hydrochloric acid >

Sodium chloride > Thiourea

Thus, nitric acid and hydrochloric acid were the best passivators of Inconel (600) in sulphuric acid.

The Transpassive State

This covers the D-E region of the polarization curve in Fig. (1) and may represent the region at which pitting of the alloy commences. Thus, the pitting potential (E_p) did not alter significantly when nitric acid, thiourea or sodium chloride or hydrochloric acid were present in H₂SO₄ solution.

The pitting current density (i_p) of Inconel (600) in sulphuric acid decreased when nitric acid was present. A similar effect was observed when 10^{-3} mol.dm⁻³ of either thiourea or sodium chloride was added to sulphuric acid. With all the other concentrations of thiourea and sodium chloride i_p became higher than that when these substances were absent. Hydrochloric acid had also an enhancing effect on i_p value of the alloy in sulphuric acid. Thus, the rate of pitting diminishes considerably by the presence of nitric acid, at any concentration, and also by relatively low concentrations of thiourea and sodium chloride (Table (2)).

Kinetic behaviours

The dependence of the corrosion (i_c), critical (i_{cr}), passivity (i_{pas}) and pitting (i_p) current densities on temperature (T) has been examined by plotting log i against the reciprocal of temperature (1/T), a typical plot of which is shown in Fig. (2). For all the four types of current densities, the log i versus 1/T were adequately linear obeying the relation:

$$\text{Log } i_{\text{corr.}} = \log A \pm E / R T \quad (1)$$

where E is the energy of activation and A is the pre-exponential factor. Thus, values of log i either decreased or increased with the reciprocal of temperature resulting in positive or negative values of E. Values of E and A which have been derived from the slopes and the intercepts of the plots are presented in Table (3).

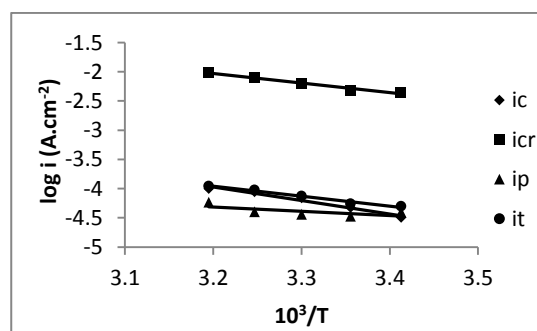


Fig. (2): Values of log i plotted against 1/T for Inconel (600) in 1 mol.dm⁻³ of H₂SO₄ solution.

Thiourea enhanced considerably the activation energy of corrosion from 40 to 70 kJ.mol⁻¹ while nitric acid, sodium chloride and hydrochloric acid lowered the activation energy of the alloy corrosion in sulphuric acid. This reflects the greatest inhibiting effect of thiourea as compared with the three other substances. The pre-exponential factor (A) increased by the addition of nitric acid, thiourea and hydrochloric acid but decreased only by the presence of sodium chloride in sulphuric acid. The increase or decrease of A by the presence of a substance in the corrosion medium is attributed to the variation of

the entropy of activation for the corrosion process.

For critical state values of $\log A$ which are reported in Table (3) did not differ appreciably than that obtained for Inconel in the H_2SO_4 solution of 18 $\text{atm.cm}^{-2}.\text{s}^{-1}$. Values of E obtained by the addition of sodium chloride and hydrochloric acid to sulphuric acid were close to that for the alloy in the acid solution of 20 kJ.mol^{-1} . Addition of nitric acid or thiourea resulted in negative energies of activation. Since

values of E are apparent (E_{app}), one would expect such negative values if enthalpies of corrosion (ΔH), which contribute to the true energy of activation (E_{true}), are appreciably exothermic in agreement with the relation:

$$E_{\text{app}} = E_{\text{true}} + \Delta H \quad (2)$$

Such a relation holds particularly when the corrosion reaction and anodic dissolution process fits to a first-order kinetics [5].

Table (3): Activation energies (E) and pre- exponential factors (log A) for the corrosion, critical, passivity and pitting of Inconel (600) in 1M sulphuric acid over the temperature range 293-313 K in the absence and the presence of some other substances of concentration (C).

State	Substance present	C (mol.dm ⁻³)	E (kJ.mol ⁻¹)	Log A (atm.cm ⁻² .s ⁻¹)
Corrosion	—	—	40	22
	Nitric acid	10 ⁻³ .10 ⁻¹	27	27
	Thiourea	10 ⁻³ .10 ⁻¹	70	26
	Sodium chloride	10 ⁻³ .10 ⁻¹	32	19
	Hydrochloric acid	10 ⁻²	38	29
Critical	—	—	20	19
	Nitric acid	10 ⁻³ .10 ⁻¹	-8	20
	Thiourea	10 ⁻³ .10 ⁻¹	-28	21
	Sodium chloride	10 ⁻³ .10 ⁻¹	18	19
	Hydrochloric acid	10 ⁻²	15	20
Passivity	—	—	10	20
	Nitric acid	10 ⁻³ .10 ⁻¹	38	18
	Thiourea	10 ⁻³ .10 ⁻¹	38	19
	Sodium chloride	10 ⁻³ .10 ⁻¹	41	18
	Hydrochloric acid	10 ⁻²	-15	18
Pitting	—	—	30	18
	Nitric acid	10 ⁻³ .10 ⁻¹	28	19
	Thiourea	10 ⁻³ .10 ⁻¹	10	18
	Sodium chloride	10 ⁻³ .10 ⁻¹	19	20
	Hydrochloric acid	10 ⁻²	-10	19

Table (3) presents the activation energy necessary for the anodic polarization process at which occurs the formation of the passive film. For Potential values greater than the Flade potential (point C in Fig. (1)) the rate of anodic dissolution decreases greatly (Table (2)), the dissolution current (i_{pas}) sinking to low values (10^{-4} - 10^{-6} A.cm^{-2}); this is the passive state. The existence of low anodic dissolution current (i_{pas}) shows that the passive layer is still dissolving, even in the potential range corresponding to passivity. The dissolution is extremely slow and occurs

almost at a constant rate over the whole passive range.

Values of E for the passivation of Inconel (600) in sulphuric acid (Table (3)) increased considerably by the addition of nitric acid, thiourea and sodium chloride but decreased considerably by the presence of hydrochloric acid. The passive layer formed on Inconel (600) is thus much easier to dissolve than the passive layer formed on pure nickel (78.8 kJ.mol^{-1}).

On the D-E section of the potentiostatic curve (Fig. (1)) there follows a very marked increase of the anodic

dissolution current (i_p), showing that the passive film suffers a strong dissolution process at a potential equal or greater than E_p (Table (2)). The activation energy for pitting and transpassive processes (30 kJ.mol^{-1}) is much higher than that for passivation (10 kJ.mol^{-1}) due to the lowering of the corrosion rate (i_p) and its larger dependence on temperature. The energy of activation for pitting decreased by the addition of thiourea, sodium chloride and more substantially by hydrochloric acid. Values of the pre-exponential factor (A) for all the four types of processes (Table (3)), involving corrosion, critical, passivity and pitting were generally close to the value of A for Inconel (600) in the H_2SO_4 solution. Thus, addition of such substances as nitric acid, affected mainly the energy of activation of the various reactions. This implies an almost similar activation process involving almost the same entropy of activation.

Conclusions:

The tendency for corrosion of Inconel (600) in sulphuric acid as predicted from the respective corrosion potentials increased generally in the presence of nitric acid but decreased in the presence of thiourea, sodium chloride or hydrochloric acid in the sulphuric acid solution. Thiourea caused the greatest decrease in the corrosion tendency of Inconel (600) in sulphuric acid solution. Thiourea and hydrochloric acid caused a shift in E_{cr} to more noble potentials decreasing the tendency of the alloy to attain the critical state considerably. On the other hand, the critical current density (i_{cr}) increased considerably by the addition of thiourea, nitric acid, hydrochloric acid and sodium chloride. The change of E_{pas} value was somehow greater by the addition of thiourea and hydrochloric acid and the shift was towards more noble potentials. The passive current density (i_{pas}) generally

decreased when other substances were present in sulphuric acid except for the higher thiourea concentrations (1×10^{-2} , 1×10^{-1}) mol.dm^{-3} . The decrease in the value of i_{pas} was substantial when nitric or hydrochloric acid was present in the sulphuric acid. The pitting potential (E_p) did not alter significantly when nitric acid, thiourea or sodium chloride or hydrochloric acid were present in H_2SO_4 solution. The rate of pitting (or pitting current density (i_p)) diminishes considerably by the presence of nitric acid, at any concentration, and also by relatively low concentrations of thiourea and sodium chloride. Thiourea enhanced considerably the activation energy of corrosion while nitric acid, sodium chloride and hydrochloric acid lowered the activation energy of the alloy corrosion in sulphuric acid. This reflects the greatest inhibiting effect of thiourea as compared with the three other substances.

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تآكل، سلبية و نقر سبيكة الانكونيل (600) في حامض الكبريتيك

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الخلاصة

أجريت دراسة مجهادية سكونية لسلوك سبيكة الانكونيل (600) في محلول حامض الكبريتيك المولاري على مدى درجات الحرارة من 293 إلى 313 كلفن. أمكن الحصول على قيم جهود وكثافات تيار التآكل والحالة الانتقال من الإيجابية الى السلبية والحالة السلبية وما بعد السلبية. أمكن إيجاد جهد التآكل (E_c) وكثافة تيار التآكل (i_c) من تقاطعات خطوط تافل. تم إيجاد الجهد الحرج (E_{cr}) وكثافة التيار الحرج (i_{cr}) للتحويل من الحالة الإيجابية إلى السلبية. وأمکن تحديد مدى السلبية بدلالة جهود وكثافات تيار تكوين وذوبان طبقة السلبية. نقطة ذوبان طبقة السلبية قد تم ربطها بجهد (E_t) وكثافة تيار (i_t) نقطة ما بعد السلبية. إن جميع قيم الجهود وكثافات التيار كانت تتأثر بدرجة الحرارة وبوجود المضافات في وسط التآكل. فالمضافات مثل حامض النتريك والثايورييا وكوريد الصوديوم سببت خفضاً في قيمة كثافة تيار التآكل (i_c) للسبيكة في حين أدت إضافة حامض الهيدروكلوريك إلى وسط التآكل إلى زيادة قيمة i_c . أدت إضافة كل من الثايورييا أو كلوريد الصوديوم أو حامض الهيدروكلوريك إلى إزاحة جهد التآكل (E_c) إلى قيم أقل سالبة في حين أزاحت إضافة حامض النتريك جهد التآكل (E_c) إلى قيم أكثر سالبة. اقتصرت التأثيرات الحركية للمضافات المختلفة على قيمة طاقة تنشيط التآكل. اعتبرت قيم طاقات التنشيط المستحصلة بأنها قيم ظاهرية وكانت بعضها سالبة.

الكلمات المفتاحية: دراسة مجهادية، منحنى الاستقطاب، الحالة الحرجة، الحالة السلبية، الحالة ما بعد السلبية.