Corrosion Inhibition of inconel (600) In Sodium Chloride solution by Sodium sulphate

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ABSTRACT

A potentiostatic investigation has been carried out of the corrosion behaviour of Inconel (600) in chloride ions(Cl^-) over the temperatures293 to 308 K.The work also involved the examination of the inhibiting effects of sodium sulphate on the corrosion of the alloy in chloride ions ,Such changes were examined in both the deaerated and oxygenated atmospheres .The presence of sodium sulphate in the chloride solution caused a decrease in the corrosion current density and a shift in the corrosion potential towards less negative values . Values of the kinetic parameters , and of the thermodynamic quantities of inconel corrosion in chloride ion in both deaerated and oxygenated atmospheres in the absence and the presence of sodium sulphate have been determine. The corrosion reaction was generally feasible on thermodynamic grounds .The kinetic results on inconel (600) occurred on surface sites having different energies of activation.

INTRODUCTION

Nickel is important as an alloy addition and as a base material for corrosion resistance alloys (1-4). Inconel (600) has a high degree of resistance to corrosion in atmosphere when exposed to fresh and natural water, and the alloy exhibits little tendency to breakdown even in acidic solution containing 1N sodium chloride (5-7). Because of the high resistance of inconel (600) to corrosion in high purity, it is quite frequently used in nuclear reactors for steam generator tubing and water piping (5).

They have been numerous investigations on the effect of the organic acids on the anodic dissolution of nickel alloys (8). Some attempts have been made (9-10) to determine the effect of sea –water and copper chloride on pitting of inconel (600).

Pervious studies also covered the effect of sulphate and phosphate ions on the pitting potential of inconel (600) in 0.1 M NaCl solution at elevated temperatures. The present paper involves a potentiostatic corrosion investigation of an important nickel alloy (inconl 600) in sodium chloride solutions in the absence and the presence of sodium sulphate. The latter has been selected to inhibit the corrosion behaviour of the alloy in NaCl solution.the experiments have been performed under nitrogen atmosphere as well as in oxygenated condition in an attempting to understand the influence of oxygen onset and extent

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of the metal .No such has so far been reported in the literature

Experimental

Inconel (600) was used in this investigation spectroscopic analysis of the alloy indicated the composition in weight percentages

Element Ni Cr Fe C Mn Si

Wt % 0.76 15.5 8 . 0.08
0.5 0.25

Sodium chloride and sodium sulphates were annular samples obtained form B.D.H. The cell assembly consisted of working, the platinum auxiliary and saturated calomel electrodes, which have been immersed in 750 ml of the test solution .The temperature of the solution was controlled to within 0.01C. Deionized water was used for the preparation of the cell solution.

The working electrode, which was made form the inconel-600 specimen, was cylindrical and the exposed area to the corrosion medium was circular in shape with diameter of 2.5 cm. The reference calomel electrode via aLuggin capillary bridge, which was usually filled with test solution.

The polarization curve was obtained using a potentiostat, type part 10-0.5L,which was obtained form Tacussel (11), France. Both the cathodic and anodic current –potential curves were obtained by decreasing or increasing polarization. The potential scan began initially after the specimen immersion in the test solution beginning at- 1.5 volt and proceeded through to +1.2 volt. A potentiodynamic sweep rate of 15 mv/min was used recording the current density continuously with the change of potential.

The surface preparation procedures of the working electrode and the experimental techniques utilized have been described elsewhere (12-13). The experiments have been performed usually under pure nitrogen gas. In series of experiments the NaCl solution, prior to the immersion of the working electrode, was purged for a minimum of 2 hours with pure (99.9pure) oxygen gas at a rate of 150 cm^3 per minute.

The anodic (ba) and cathodic (bc) Tafel slopes of the tangents have been drawn to the corresponding Tafel lines (13-14) have been determined form he polarization curves. The corrosion potential (Ec) and the corrosion current density (ic) has been obtained form the point of intersection of the anodic and cathodic Tafel lines using the 4-point method (14).

T/K	Deaerated						Oxygenated					
	-Ecorr/ V	I corr Acm^{-2}	-bc- Vdecade^{-1}	ba Vdecade^{-1}	α C	α a	-Ecorr/ V	I corr Acm^{-2}	-bc- Vdecade^{-1}	ba/ Vdecade^{-1}	α C	α a
293	0.98	5.7 X10^{-6}	0.112	0.100	0.582	0.582	0.19	7.2X10^{-7}	0.085	0.096	0.684	0.605
298	0.96	7X10^{-6}	0.118	0.110	0.547	0.537	0.25	4.8X10^{-6}	0.100	0.093	0.591	0.636
303	0.95	8.5X10^{-6}	0.120	0.115	0.501	0.523	0.29	7.5X10^{-6}	-----	0.090	------	0.668
308	0.93	9.2X10^{-4}	0.123	0.118	0.496	0.517	0.32	8.4X10^{-6}	0.102	0.082	0.599	0.745

Table:(1): Values of Corrosion current densities (icorr) and corrosion potential (Ecorr), Tafel slope and Transfer of inconel in deaerated and oxygenated solution of 0.5 M NaCl solution at four temperature.

Results and Discussion

1-Polarization behaviour:

Table 1 give values of the corrosion potential (Ec) and corrosion current density (ic) for the corrosion of inconel (600) in chloride solution in both deaerated and oxygenated atmospheres in the absence and the presence of sodium sulphate at four temperatures in the range 293 -308 K. A general increase in the corrosion current density with increasing temperature has been observed, it appears from the previous data that the overall anodic behaviour of inconel in deaerated and oxygenated solution. Values of Ec became more negative with increasing temperature in deaerated solution as shown in fig (1). This reflects the increasing tendency of inconel for corrosion with temperature. Similar behaviour was noticed in the presence sodium sulphate in deaerated and oxygenated media. Table (1) lists values of icorr and Ecorr for the corrosion of the alloy in NaCl solution in the presence of 0.05-mol $dm^{-3}$of Na_2SO_4 in deaerated and oxygenated solution.

2-Inhibiting Effect of Na_2SO_4

The corrosion current density (ic) in the presence $(ic)_2$ and absence $(ic)_1$ of Na_2SO_4 in the chloride solution at constant temperature have been used to determine the protection efficiency (in percentage p%) of the $NaSO_4$ from the relation(13,15) ;

$P\% = 100(1-(ic)_2/(ic)_1)$ ----------------- (1)

The results of P% values in deaerated and oxygenated media at the various experimental temperatures are inserted in table 2. Values of P% in all cases exceeded 90 .Such high efficiency of Na_2SO_4 for corrosion inhibition of inconel 600in chloride solution in the both deaerated and oxygenated atmospheres .

3-Kinetics of corrosion

The rate of corrosion, as expressed (13,15) by the corrosion current density (ic), increased generally with the rise of temperature in a manner which followed Arrhenius equation: -

$Ic = A \exp(-E/RT)$------------------(2)

Where A is the pre- exponential factor and E is the energy of activation. Values of E and A for he corrosion reaction have been derived form the slopes and intercept of log versus 1/T plots as indicated in fig (2). Values of A which have been derived form such plots have been expressed in $A\ m^{-2}$ which have been converted into units of atom $m^{-2}\ s^{-1}$. Table (3)gives values of A and E for the corrosion of inconel 600 in deaerated and oxygenated chloride solution in the absence and the presence of Na_2SO_4.

The activation energies (E) of corrosion were generally lower in the deaerated solution than in the oxygenated solution. in the absence sodium sulphate .E did alter significantly even in the inhibitor in deraerated and oxygenated solution.

The variation of log A values remained generally similar to those of E in deaerated or oxygenated solution in the absence or the presence of inhibitors. This suggests the existence of direct relationship between the values of Ea and the corresponding values of log A(15) .Such a behaviour is referred to as " compensation effect" which describes the kinetics of a great number of catalytic and tarnishing reaction metals(14,15) . Equation (2) indicates that simultaneous increase or decreases in E and log A for a system tend to compensate form the standpoint of the reaction rate.

4-Thermodynamics of corrosion

The change in the Gibbs free energy (ΔG) of corrosion was calculated as (14):

$\Delta G = -nFE$ ---------------(3)

Where F is the Faraday constant , n the number of electrons which were involved in the corrosion reaction and Ec is the corrosion potential (in volt) .The equation indicates that Ec is directly proportional with Gibbs free energy (ΔG) of the corrosion reaction

The change in the entropy of corrosion reaction (ΔS) may be determined from the values of (ΔG) which are obtained at several experimental temperatures according to the well-known thermodynamic relation (15).

$$-d(\Delta G/dT)=\Delta S\text{---------}(4)$$

The change in the enthalpy of corrosion (ΔH) may then be obtained using the corresponding values of ΔG and ΔS according to:

$$\Delta H=\Delta G+T\Delta S\text{------}(5)$$

The results of tables (4) and (5) reflect the thermodynamic feasibility of the corrosion reactions of inconel in chloride solution.

Values of (ΔG)for the corrosion of inconel in the absence and the presence of inhibitor in the deaerated solution ,range 179 to 212 kj mol^{-1}.In the oxygenated medium ,the values of ΔG ranged form 36 to 108 kj mol^{-1}.

This reflects the decreasing feasibility of inconel (600) for corrosion in the presence of sodium sulphate in deaerated medium in the NaCl solution. Values of ΔS were positive or negative depending on the positive or negative depending of ΔG values on temperature. Values of ΔS in table (4) and (5) reflect the changes in the order and orientation of the solvent molecules around the hydrated metal ions resulting in the corrosion process. Generally, the values of ΔS were less negative oxygenated medium as compared with the case in deaerated medium.

The ΔS values in table (4) and (5), which were associated with the inhibitor addition to the corrosion medium had somewhat more negative of freedom through out the adsorption of the inhibitor on inconel alloy. The enthalpy changes ΔH for corrosion reaction of inconel (600) ranged form negative to positive values indicating exothermic or endothermic nature of corrosion reaction. Values of ΔH varied in the presence of sodium sulphate reflecting the variation in the strengths of inhibitor of inhibitor adsorption on the alloy surface.

Table:(1): Values of Corrosion current densities (icorr) and corrosion potential (Ecorr), Tafel slope and Transfer of inconel in deaerated and oxygenated solution of 0.5 M NaCl solution at four temperature.

Table :(2): Effect of inhibitor concentration Sodium Sulphate (0.05 mol dm^{-3}) for inconel in deaerated and oxygenated solution of 0.5 mol dm^{-3} of NaCl solution at four temperature.

T/K	Deaerated							Oxygenated						
	-Ecorr/ V	I corr/ Acm^{-2}	-bc- $Vdecade^{-1}$	-ba/ $Vdecade^{-1}$	α C	α a	P%	-Ecorr/ V	I corr/ Acm^{-2}	-bc- $Vdecade^{-1}$	-ba/ $Vdecade^{-1}$	α C	α a	P%
293	0.95	$7.9X10^{-7}$	0.058	0.058	0.855	[illegible]	86.2	0.56	$5.1X10^{-8}$	0.129	0.082	0.455	0.709	92.9
298	1.06	$1.27X10^{-6}$	0.06	0.954	0.980	0.055	81.8	0.53	$1X10^{-7}$	0.196	0.076	0.3019	0.778	97.9
303	1.08	$1.9X10^{-6}$	0.055	0.062	1.09	0.97	[illegible]	0.51	$2.8X10^{-7}$	0.120	0.075	0.501	0.801	96.3
308	1.1	$2.85X10^{-6}$	[illegible]	[illegible]	—	0.942	55.9	0.49	$3.1X10^{-7}$	0.118	0.072	0.517	0.848	96.3

Table: (3) : :Values of activation energies (E kJ mol^{-1}) and pre-exponential factors(A/molecules m^{-2} s^{-1}) for the corrosion of **inconel inabsence** and presence sodium sulphate in deaerated and **oxygenated solution at298k.**

In absence Na_2SO_4				In presence Na_2SO_4			
Deaerated		Oxygenated		Deaerated		Oxygenated	
E/ kJ mol^{-1}	A	E/ kJ mol^{-1}	A	E/ kJ mol^{-1}	A	E/ kJ mol^{-1}	A
24.1[illegible]	[illegible]	27.36[illegible]	[illegible]	53.77	$9.1x10^{23}$	88.9	$2.37X10^{27}$

Table (4) : Values of the thermodynamic (ΔG, ΔS and ΔH) for the corrosion of the Inconel in 0.5 mol dm^{-3} Nacl in deaerated and oxygenated

	Deaerated			Oxygenated		
T/K	$-\Delta G$-/kJ mol^{-1}	ΔS/Jmol^{-1}K^{-1}	ΔH/kJmol^{-1}	$-\Delta G$-/kJ mol^{-1}	ΔS/Jmol^{-1}K^{-1}	ΔH/kJmol^{-1}
293	189.14		-0.741	36.676		-526.5
298	185.28	643	6.264	48.25	-1672	-546.5
303	183.35		11.479	55.97		-562.59
308	179.49		18.554	61.76		-576.73

	Deaerated			Oxygenated		
T/K	$-\Delta G$-/kJ mol^{-1}	ΔS/Jmol^{-1}K^{-1}	ΔH/kJmol^{-1}	$-\Delta G$-/kJ mol^{-1}	ΔS/Jmol^{-1}K^{-1}	ΔH/kJmol^{-1}
293	183.35		-0.748.84	108.08		155.62
298	204.58	-1930	-779.72	102.29	900	165.91
303	208.44		-793.23	98.43		178.27
308	212.30		-806.74	94.57		187.13

Table :(5): Values of the thermodynamic (ΔG, ΔS and ΔH) for the corrosion of Inconel in presence 0.05mol dm^{-3} Na_2SO_4 of in deaerated and oxygenated of NaCl 0.5 mol dm^{-3} Solution.

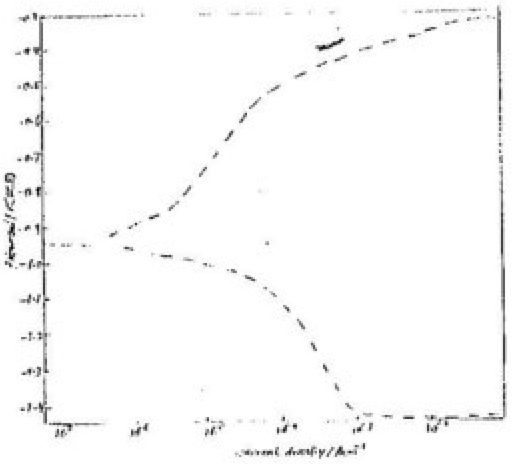

Fig.-1- A typical polarization curve for the corrosion of inconel 600 in deaerated 0.5 mol dm⁻³ NaCl at 303 K

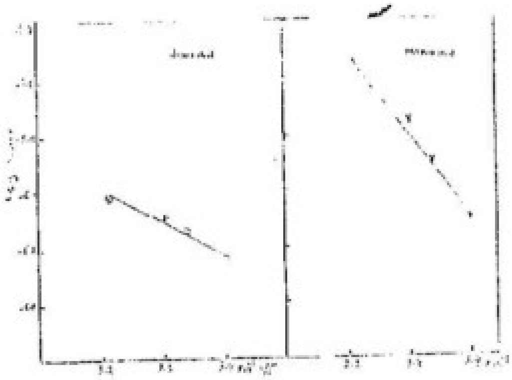

Fig 2: Arrhenius plots, relating log Icorr with 1/T, for the corrosion of inconel 600 in 0.5 mol dm⁻³ of Sodium chloride solution

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تنشيط التآكل للانكونيل (600) في محلول كلوريد الصوديوم بواسطة كبريتات الصوديوم

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الخلاصة

تمت دراسة السلوك التاكلي للانكونيل (600) في محلول كلوريد الصوديوم في المدى 293 الى 308 كلفن باستخدام تقنية المجهاد السكوني . تضمن البحث ايضا التأثير التثبيطي لكبريتات الصوديوم في محلول كلوريد الصوديوم بوجود النايتروجين او الاوكسجين على سبيكة الانكونيل (600) ، فقد تبين من الدراسة ان وجود كبريتات الصوديوم سبب في نقصان كثافة التيار وانحراف الجهد باتجاه القيم الاقل سالبية وحسب ان تفاعل التآكل يحدث على مواقع متباينة على سطح السبيكة من حيث قيم طاقة التنشيط .