



Evaluation of Resistance Offered by 304 Stainless Steel Alloy Against Corrosion and Pitting in H_3PO_4 -HCl Medium by Determination and Study of Corrosion Resistance Parameter

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Abstract: Parameter for evaluation of resistance offered by 304 stainless steel alloy against corrosion and pitting in H_3PO_4 -HCl medium is suggested. Parameter has been calculated on the basis of anodic parameters obtained from potentiodynamic polarization curves. Corrosion resistance parameter (R_p) is found to vary with change in temperature and with change in concentration of HCl.

There is found to be direct relationship between R_p and pitting attack on alloy surface. The minimum value of R_p above which presence of chloride ions in the form of HCl may be tolerated without undergoing pitting attack is dependent on temperature of the medium. At a fixed temperature there is a minimum value of R_p below which pitting starts depending on concentration of HCl in the medium.

Key words: Stainless steel, corrosion, phosphoric acid, corrosion resistance, anodic parameters.

I. Introduction

Austenitic stainless steels are extensively used as construction material of containers during production, storage and transport of phosphoric acid. Phosphoric acid is utilized in production of phosphatic fertilizers on a large scale. Stainless steels offer good corrosion resistance in pure phosphoric acid but in practical situations phosphoric acid is often contaminated with small amounts of aggressive ions in the form of HCl. Hydrochloric acid as an added impurity enters into phosphoric acid as an added impurity during its production by acidulation process.

In presence of phosphoric acid-HCl medium, stainless steel 304 SS loses its corrosion resistance i.e., ability to withstand this particular environment without undergoing disintegration due to the presence of aggressive ions and often undergoes pitting attack. This limits the utilization of this important alloy in the studied medium. Studies have been conducted earlier to study pitting and stress corrosion of other stainless steel alloys in other mediums [1, 2] but studies on 304SS in phosphoric acid-HCl medium are rare. The present work involves the evaluation and study of corrosion resistance parameter in case of 304SS in concentrated phosphoric acid at different concentrations of HCl and at different temperatures.

II. Experimental

The composition of 304 SS was 18Cr, 10Ni, and balance Fe. The electrode system consisted of austenitic stainless steel working electrode, a counter electrode of platinum and saturated calomel electrode with KNO_3 salt bridge. Electrochemical experiments were conducted in an air thermostat maintained at 298, 308 and 318 K under still condition. The solution contained 14M phosphoric acid with different concentrations of HCl present in it.

Potentials were impressed on the working electrode of area 1cm^2 by a fast rise power potentiostat Wenking Model POS 73. Potentiodynamic polarization curves were recorded starting from open circuit potential with a scan rate of $1\text{mV}\cdot\text{sec}^{-1}$.

Anodic polarization curves are of a similar nature independent of HCl concentration and temperature [3]. General nature of curves is an active zone followed by a passive region which enters into transpassive region at nobler potentials. Anodic parameters i.e., passivation potential (E_p), passive current density (i_p) and breakdown potential (E_b) are found out from anodic polarization curves and are shown in Table 1, 2 and 3 at 298, 308 and 318 K respectively. Newly introduced parameter R_p is also calculated at various concentration of HCl in 14M phosphoric acid medium. Table-4 shows corrosion resistance parameter R_p at 298, 308 and 318 K.

III. Result and Discussion

It is observed from anodic polarization curves that passivation starts at E_{pp} and is completed at E_p . If the potential is increased beyond E_p current density does not increase rather it remains constant till E_b is approached.

It is witnessed from SEM analysis of stainless steel samples that in the range of potential E_p to E_b passive film is present on alloy surface.

Passivity continues throughout the passive range of potential (E_p to E_b) and breakdown of passive film occurs at E_b . Passive film formation is influenced by concentration of chloride ions and temperature of medium leading to variation in the quality (composition and porosity) of passive film. Resistance offered by passive film against corrosion is decided by the difference between the rate of formation of vacancies and their disappearance in the bulk [4]. During passive range of potential, rate of formation of vacancies is compensated by the rate of their disappearance in the bulk. At E_b and beyond E_b , rate of formation of vacancies exceeds the rate of their disappearance in bulk hence cation vacancies start piling up creating a void leading to the formation of holes (pits).

As passivity is maintained in the potential ranging from E_p to E_b , the change in resistance offered by the alloy in the range E_p to E_b decides the resistance offered by the alloy against pitting corrosion.

Change in resistance of alloy (resistance offered by the passive film) in the range E_p to E_b is given by

$$R_p = (E_b/i_p) - (E_p/i_p) \\ = (1/i_p) \{E_b - E_p\}$$

As $R = k R_p$

Where R_p is the resistance offered by passive film against corrosion, R is corrosion resistance and k is a constant.

Thus,

$$R = K \{E_b - E_p\}/i_p$$

From anodic polarization curves it is clear that passive range ($E_b - E_p$) is a measure of potential to be increased to nobler values so that passive state is lost and localized breakdown of passive film starts. Hence the range of potential from E_p to E_b decides the extent of resistance offered by alloy against localized corrosion. Larger is the range, greater is the resistance offered by the passive film.

Hence, $R_p \propto E_b - E_p$

Passive current density (i_p) is the current flowing through the passive film [5]. With increase in the concentration of HCl in the medium i_p is found to increase. Variation of passive current density (i_p) with concentration of HCl is attributed to the presence of chloride ions in the medium which compete with oxide ion adsorption at film-solution interface creating defects in passive film. At higher concentration of chloride ions possibility of formation of metal-halide complexes is more thus resulting in increase in defect density in the passive film. At higher temperature chemisorption of chloride ions is facilitated leading to more defective passive film thus increasing the i_p value. Alloy with a passive film having more defect density is prone to suffer localized attack and to undergo corrosion in comparison to alloy having a compact passive film. Hence resistance offered by 304SS in presence of a certain concentration of halide ions depends on i_p which in turn depends on compactness of passive film i.e. whether it is with defects or without defects.

$$R_p \propto 1/i_p$$

Resistance offered by the alloy against corrosion [6] and pitting is related to passive range in the potentiodynamic polarization curves i.e. $E_b - E_p$ as is reported elsewhere [5].

$$R = K R_p$$

Where K is a constant.

R_p is proportional to $E_b - E_p$.

R_p is inversely proportional to i_p

$$\text{Hence } R_p = K (E_b - E_p)/i_p$$

Taking this into account R_p is assigned the name "corrosion resistance parameter" and its values have been calculated from anodic parameters i_p , E_b and E_p .

Values of corrosion resistance parameter (R_p) are shown in Table1, 2 and 3. There is found to be a decrease in corrosion resistance (R_p) with increase in concentration of HCl at 298 K. Similarly at 308 and 318 K also decrease in corrosion resistance (R_p) is observed with increase in concentration of HCl in the medium.

Up to 4000 ppm of HCl concentration, temperature effect shows a regular trend. Corrosion resistance decreases by $1/15^{\text{th}}$ to $1/20^{\text{th}}$ with rise in temperature from 298 to 308 K whereas it is reduced to $1/2$ with rise in temperature from 308 to 318 K at a fixed concentration of HCl. Critical concentration values of HCl above which pitting starts at a particular temperature is reported elsewhere [3]. Critical concentration of HCl beyond which pitting starts is found to change by a greater magnitude (7600 to 3800ppm HCl) in the temperature range 298 – 308 K in comparison to change in critical concentration from 3800 to 2900 ppm HCl in the temperature range 308 to 318K.

In lower concentration range (1000ppm to 4000ppm) of HCl concentration R_p shows a large decrease as the temperature is raised from 298 to 308 K whereas the decrease is by a smaller magnitude for temperature change from 308 to 318 K. It is found that at 298 K if corrosion resistance R_p attains a value below 7.3Ω pitting starts. The minimum value of corrosion resistance below which pitting corrosion is observed is found to be 0.2Ω and 0.1Ω at temperatures 308 and 318 K respectively. It is inferred from the results that the minimum value of

resistance below which pitting starts shows a greater shift in 298-308 K temperature range than in 308-318 K range.

IV. Conclusion

Susceptibility of alloy 304SS towards localized corrosive attack increases with increase in concentration of HCl and temperature as was observed earlier [7]. Similar result reflecting dependence of susceptibility of another stainless steel alloy towards pitting has been reported earlier [5]. Mathematically evaluated corrosion resistance parameter also shows decrease with increase in HCl concentration and temperature. A greater increase in susceptibility to corrosive attack is observed from the variation of corrosion resistance parameter (R_p) when temperature is raised from 298 to 308 K in comparison to that observed when temperature is raised from 308 to 318 K.

Critical concentration of HCl beyond which pitting starts and minimum value of R_p below which pitting starts are found to show a greater shift in 298 to 308K range than in higher temperature range (308 – 318 K). Corrosion resistance evaluated mathematically using equation $R = K (E_b - E_p) / i_p$ is a measure of resistance offered by stainless steel alloy 304SS as is found from agreement between experimental observation and theoretical calculation.

Table -1 Anodic parameters of AISI 304 SS in 14 M phosphoric acid at 298 K having different concentrations of HCl.

Concentration of HCl (ppm)	I_p (mA.m ⁻²)x10 ⁴	E_p (mV)	E_b (mV)	$E_b - E_p$ (mV)	R_p ($E_b - E_p / i_p$) (Ω .m ⁻²)
Blank solution	0.004	-180	1130	1310	32.8
1000	0.006	-120	950	1070	17.8
2000	0.008	-100	940	1040	13.0
3000	0.008	-60	920	980	12.3
4000	0.010	-30	910	940	9.4
5000	0.012	+30	900	870	7.3
10000	0.020	+80	690	610	3.1
15000	0.060	+100	680	580	0.9
20000	0.150	+120	680	560	0.4

Table -2 Anodic parameters of AISI 304 SS in 14 M phosphoric acid at 308 K having different concentrations of HCl.

Concentration of HCl (ppm)	I_p (mA.m ⁻²)x10 ⁴	E_p (mV)	E_b (mV)	$E_b - E_p$ (mV)	R_p ($E_b - E_p / i_p$) (Ω .m ⁻²)
Blank solution	0.02	-190	1130	1320	6.6
1000	0.10	-180	980	1160	1.2
2000	0.16	-180	970	1150	0.7
3000	0.24	-200	950	1150	0.5
4000	0.63	-80	615	695	0.1
5000	1.00	-60	605	665	0.07
10000	1.58	+50	560	510	0.03
15000	1.73	+70	500	430	0.02
20000	0.90	+80	460	380	0.02

Table -3 Anodic parameters of AISI 304 SS in 14 M phosphoric acid at 318 K having different concentrations of HCl.

Concentration of HCl (ppm)	I_p (mA.m ⁻²)x10 ⁴	E_p (mV)	E_b (mV)	$E_b - E_p$ (mV)	R_p ($E_b - E_p / i_p$) (Ω .m ⁻²)
Blank solution	0.06	-200	1100	1300	2.2
1000	0.14	-180	850	1030	0.7
2000	0.20	-180	840	1020	0.5
3000	0.63	-60	600	660	0.1
4000	0.76	-50	560	610	0.08
5000	1.20	-50	530	580	0.05
10000	1.72	+40	430	390	0.02
15000	2.00	+80	310	230	0.01
20000	2.40	+100	260	160	0.01

Table-4: Variation of corrosion resistance (R_p in $\Omega \cdot m^{-2}$) with concentration of HCl at various temperatures.

Concentration of HCl (ppm)	Corrosion resistance (R_p) at		
	298K	308K	318K
1000	17.8	1.2	0.7
2000	13.0	0.7	0.5
3000	12.3	0.5	0.1
4000	9.4	0.1	0.08
5000	7.3	0.07	0.05
10000	3.1	0.03	0.02
15000	0.9	0.02	0.01
20000	0.4	0.02	0.01

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