



International Journal of Emerging Technologies in Computational and Applied Sciences (IJETCAS)

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A comparative study of resistance offered by different stainless steel alloys against corrosion and pitting by determination and study of corrosion resistance parameter

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Abstract: Corrosion resistance parameter (R_p) is determined and studied in case of stainless steels bearing different alloying elements at 298K. Corrosion resistance parameter is calculated on the basis of anodic parameters obtained from potentiodynamic polarization curves. R_p is found to vary depending on the type of minor alloying element present as constituent of steel.

There is found to be direct relationship between R_p and occurrence of pitting attack on alloy surface. Minimum value of R_p below which pitting occurs is found to be dependent on the minor alloying element present, being lowest for 316SS (molybdenum bearing stainless steel). At a fixed value of HCl concentration, R_p is found to show dependence on alloy composition reflecting that corrosion resistance offered by steels follows the order, 316SS > 321SS > 304SS.

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

I. Introduction

Chromium and nickel alloyed stainless steels are known to offer good corrosion resistance in pure phosphoric acid making them most suitable alloy to be utilized as construction material of containers during production, storage and transport of phosphoric acid. The ability of alloy steels to form passive film is the basis of corrosion resistance offered by these steels. However problems are often faced as in practical situation phosphoric has some amount of aggressive ions present in it which enter into phosphoric acid during its production.

It may be realized from the results presented previously [1] that corrosion resistance parameter shows a decrease with increase in content of HCl in 14M phosphoric acid reflecting that 304SS loses corrosion resistance and becomes more susceptible to corrosion and pitting attack with increase in amount of aggressive ion in the medium. This limits the utilization of this material in the studied medium. Since pitting is basically due to imperfect state of passivity at various locations on the alloy surface the type of elements and the amount of elements constituting the alloy play a decisive role as far as deleterious attack on alloy in the form of pitting is concerned. It has been noticed that steels alloyed with chromium [2] and molybdenum [3] show a better corrosion resistance in chloride containing solutions. Passive metals such as Ti and Ti bearing alloys have been found to be stable in many environments but in certain environments such as acid solutions containing chlorides, pitting has been witnessed. Therefore much attention was given by earlier investigators to the study of pitting of passive metals and alloys [4], [5], [6], [7]. However a systematic research on corrosion and pitting of stainless steels containing Ti as a minor alloying element has not been conducted. In the present work evaluation of resistance offered by stainless steel alloyed with less than 1% Ti and the other with 3% Mo against corrosion and pitting is done. Present study is aimed at performing comparative study of resistance offered by stainless steels against corrosion and pitting under the influence of minor alloying elements Mo and Ti in terms of variation of corrosion resistance parameter.

II. Experimental

The alloys tested in this study were 304SS, 321SS and 316 SS. Composition of alloys was:

304SS	18%Cr	10%Ni	balance Fe
321SS	18%Cr	8% Ni	< 1%Ti balance Fe
316SS	18%Cr	8% Ni	3%Mo 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 298K 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 1 cm^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 were of a similar nature independent of composition of alloy and concentration of HCl [8]. General nature of curves is an active zone followed by a passive region which enters into transpassive region at nobler potentials. Various anodic parameters i.e. passivation potential (E_p), passive current density (i_p) [8] and breakdown potential (E_b) are found out from anodic polarization curves and are shown in Table 2 and 3 for 321SS and 316SS respectively. Corrosion resistance parameter (R_p) is also calculated at various concentrations of HCl in 14M phosphoric acid medium. Various anodic parameters in case of 304SS determined earlier [1] are shown in Table 1 for comparison. Table 4 shows corrosion resistance parameter (R_p) at 298K with various concentrations of HCl in case of 304SS, 321SS and 316SS.

III. Result and discussion

It was noticed from anodic polarization curves that nature of curves was similar irrespective of concentration of HCl [8] and alloy composition of stainless steels [8], [9]. General feature of anodic polarization curves with increase in potential from steady state potential is an active zone followed by a passive region which enters into transpassive region at E_b . Passive region starts at E_p and ends at E_b . Current remains constant in the range E_p to E_b and is denoted by i_p .

As introduced and discussed earlier [1] corrosion resistance parameter R_p depends on E_p , E_b and i_p following the equation,

$$R_p = K (E_b - E_p) / i_p$$

Where $E_b - E_p$ indicates the range of potential in which the rate of formation of vacancies is compensated by the rate of their disappearance in the bulk [1].

i_p is the current flowing through the passive film which depends on concentration of HCl present in the medium at a constant temperature. As discussed elsewhere [1] i_p depends on the compactness of passive film which in turn is decided by concentration of HCl in the medium. The values of corrosion resistance parameter (R_p) at 298K for 304SS, 321SS and 316SS are shown in Tables 1, 2 and 3 respectively. Corrosion resistance parameter is found to decrease with increase in HCl content in the medium irrespective of the minor alloying element Mo or Ti present in stainless steel. However the extent up to which R_p is affected by same increase in HCl content shows dependence on alloy composition. Both E_p and E_b attain nobler values when 304SS is replaced by 321SS. A greater shift in E_p and E_b towards nobler values is observed on replacing 304SS with 316SS. Passive range for the three stainless steels at any concentration of HCl is found to follow the order,

$(E_b - E_p)$ for 304SS < $(E_b - E_p)$ for 321SS < $(E_b - E_p)$ for 316SS

Passive current density (i_p) shows a decrease when 304 SS is replaced with 321SS. On replacing 304SS with 316SS a decrease by a greater amount is observed. Variation in i_p at any concentration of HCl follows the order, i_p for 304SS > i_p for 321SS > i_p for 316SS

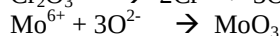
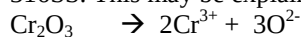
R_p is dependent on $E_b - E_p$ and i_p . It is observed from table 1, 2 and 3 that at a fixed value of HCl concentration, R_p shows an increase when 304SS is replaced with 321SS in the medium H_3PO_4 -HCl. Although R_p increases up to some extent, increase in R_p is not remarkable. An increase by a greater amount is observed in R_p when 304SS is replaced with 316SS keeping content of HCl in the electrolyte constant. R_p almost doubles when 304SS is replaced with 316SS in the studied medium at any fixed concentration of HCl. Critical concentration of HCl beyond which pitting starts also shows a greater shift (7600ppm to 14800ppm) on replacing 304SS with 316SS compared to a shift (7600ppm- 7800ppm) observed on replacing 304SS with 321SS.

Table -4 shows the variation of R_p with concentration of HCl for 304SS, 321SS and 316SS at 298K for comparison. It is observed in case of 304SS that when R_p attains a value below 7.3Ω pitting starts. The minimum value of corrosion resistance parameter R_p below which pitting starts is found to be 3.4Ω and 2.7Ω for alloy 321SS and 316SS respectively. It is inferred from the results that the minimum value of resistance below which pitting starts shows a decrease by 3.9Ω when 304SS is replaced with 321SS. It may be explained on the basis of reason given earlier by researchers that Ti present in 321SS binds carbon and nitrogen and hence prevents the formation of chromium carbides and nitrides. It minimizes the probability of creation of sites favourable for pitting attack [10].

In case of 304SS, minimum value of R_p below which pitting is witnessed is 7.3Ω which corresponds to 7600ppm HCl concentration. The corrosion resistance parameter in case of 316SS under similar environmental conditions almost doubles and is found to be 13.8Ω . Further no pitting is observed at this value of R_p in case of 316SS. At 10000ppm HCl concentration also R_p in case of 316SS is almost double of that in case of 304SS. No pitting is observed to take place on 316SS till the concentration of HCl is less than 14800ppm in the medium. R_p attains a value as low as 2.7Ω at 14800ppm HCl concentration and pitting is witnessed. Increased corrosion resistance in terms of increase in corrosion resistance parameter R_p when 304SS is replaced with 316SS may be explained on the basis of beneficial effect of Mo as an alloying element [11], [12]. When molybdenum is present as minor alloying element, molybdate ions take part in passive film formation by their adsorption on the film. This makes passive film less porous hence minimizing the chances of pitting attack [13]. Increased compactness of the film results in decreased value of i_p and increased value of corrosion resistance parameter R_p . Highly charged Mo^{6+} species interact with cation vacancies (defects) present in the film reducing cation vacancy

flux from film-solution interface to metal -film interface where the vacancies condense resulting in pit formation[14].

Under similar environmental conditions, value of R_p is increased to almost two times on replacing 304SS with 316SS. This may be explained by considering the following mechanism,



Two Cr^{3+} ions are replaced by one Mo^{6+} showing that one Mo^{6+} is sufficient for providing passivity as compared to two Cr^{3+} . Hence Mo bearing steel 316SS is twice as efficient as 304SS in offering resistance against pitting corrosion.

IV. Conclusion

It is found that susceptibility of all the stainless steel alloys to pitting corrosion increases with increase in concentration of HCl as is observed experimentally [9], [13] and from determination of corrosion resistance parameter R_p . The susceptibility of the stainless steels towards pitting corrosion depends on the presence of minor alloying element. Corrosion resistance offered by steels in terms of corrosion resistance parameter follows the order

$$R_p(316\text{SS}) > R_p(321\text{SS}) > R_p(304\text{SS})$$

At a fixed concentration of HCl corrosion resistance parameter R_p shows a greater increase when 304SS is replaced with 316SS as compared to increase in R_p observed on replacing 304SS with 321SS. This indicates that Mo has greater efficiency to offer resistance against corrosion and pitting in comparison to that offered by Ti if present as a minor alloying element. Critical concentration of HCl beyond which pitting corrosion is observed and minimum value of R_p below which pitting starts show a greater change on replacing 304SS with 316SS as compared to the change observed on replacing 304SS with 321SS. Corrosion resistance evaluated mathematically using relation, $R_p = K(E_b - E_p)/i_p$ in case of 304SS, 321SS and 316SS is a measure of resistance offered by stainless steels as is found from agreement between experimental observations and theoretical calculation.

Table-1 Anodic parameters of AISI 304SS in 14M 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 321SS in 14M 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	-170	1160	1330	33.3
1000	0.006	-100	980	1080	18.0
2000	0.006	-80	980	1060	17.7
3000	0.008	0	980	980	12.3
4000	0.008	+80	960	880	11.0
5000	0.010	+90	950	860	8.6
10000	0.018	+120	730	610	3.4
15000	0.050	+120	720	600	1.2
20000	0.090	+180	690	510	0.6

Table-3 Anodic parameters of AISI 316SS in 14M 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	0.001	-70	1250	1320	132.0
1000	0.002	-70	1190	1260	63.0
2000	0.004	-20	1180	1200	30.0
3000	0.006	+30	1170	1140	19.0
4000	0.006	+30	1150	1120	18.7
5000	0.008	+30	1130	1100	13.8
10000	0.020	+40	1100	1060	5.3
15000	0.024	+80	730	650	2.7
20000	0.030	+90	720	630	2.1

Table-4 Variation of corrosion resistance parameter (R_p) in $\Omega.m^{-2}$ with concentration of HCl at 298K.

Concentration of HCl (ppm)	Corrosion resistance parameter (R_p) for		
	304SS	321SS	316SS
1000	17.8	18.0	63.0
2000	13.0	17.7	30.0
3000	12.3	12.3	19.0
4000	9.4	11.0	18.7
5000	7.3	8.6	13.8
10000	3.1	3.4	5.3
15000	0.9	1.2	2.7
20000	0.4	0.6	2.1

References

- [1] Rita Khare, "Evaluation of resistance offered by 304SS in H_3PO_4 -HCl medium by determination and study of corrosion resistance parameter", American International Journal of Research in Science, Technology, Engineering and Mathematics, vol 2, issue 5, (2013) pp 149-152.
- [2] E.A. Lizlovs and A.P.Bond, "Anodic polarization behaviour of high purity 13 and 18 % Cr stainless steel", J.Electrochem. Soc., vol 122, (6), (1975) p 719.
- [3] H.H.Uhlig, P.Bond and H.Feller, "Corrosion and passivity of molybdenum nickel alloys in hydrochloric acid", J. Electrochem. Soc., vol 110, (6), (1963), PP 650-653.
- [4] Z.Szklarska.Smialowska, "Review of literature on pitting corrosion published since 1960", Corrosion, vol 27 (1971) p 223.
- [5] M.Janik Czachor, G.C.Wood and G.E.Thompson, "Assessment of processes leading to pit nucleation", British Corrosion Journal, vol 15,(4), (1980) p 154.
- [6] E A Ebd El Meguid and A.A.El Latiff, "Electrochemical and SEM study on type 254 SMO stainless steel in chloride solutions", Corrosion Science, vol 46, issue 12 (2004) pp 2431-2444.
- [7] E A Ebd El Meguid, N.A. Mahmood and V.K. Gouda, "Pitting corrosion behaviour of AISI 316L steel in chloride containing solutions", British Corrosion Journal, vol 33, (1), (1997) pp 42-48.
- [8] Rita Khare, M.M.Singh and A.K.Mukherjee, "The effect of addition of HCl on the corrosion behaviour of 304SS in concentrated H_3PO_4 at different temperatures", Bulletin of Electrochemistry, vol 11, (10) (1995), pp 457- 461.
- [9] Rita Khare, M.M.Singh and A.K.Mukherjee, "The effect of temperature on pitting corrosion of 316SS in concentrated phosphoric acid containing hydrochloric acid", Indian Journal of Chemical Technology, vol 9, no. 5 (2002), PP 407-410.
- [10] Mirzam Bajt Leban and Robert Tisu "The effect of TiN inclusions and deformation induced martensite on the corrosion properties of AISI 321 stainless steel", Engineering Failure Analysis, vol 33, October 2013, pp 430-438.
- [11] H.A.El Dahan, "Pitting corrosion inhibition of 316 stainless steel in phosphoric acid chloride solutions Part I, Potentiodynamic and potentiostatic polarization studies", Journal of Material Science, vol 34, issue 4 (1999) pp 851-857.
- [12] H.A.El Dahan, " Pitting corrosion inhibition of 316 stainless steel in phosphoric acid-chloride solutions part II AES investigation", Journal of Material Science, vol 34, issue 4, (1999) pp 859-868.
- [13] Rita Khare, "Surface analysis of steel samples polarized anodically in H_3PO_4 -HCl mixtures by SEM and EDAX techniques", International Journal Manthan, vol 13 (2012), pp 22-25.
- [14] D.D.Macdonald and M.Urquidi Macdonald, "Deterministic model for passivity breakdown", Corrosion Science, vol 31 (1990), p 425.

Acknowledgements

Author acknowledges the junior and senior research fellowships awarded in the Indian Institute of Technology, Banaras Hindu University, Varanasi, during conduction of experimental part of this work. Valuable suggestions from Prof. M.M.Singh and Prof. A.K.Mukherjee, Institute of Technology, B.H.U., have been providing impetus towards performing comparative study of corrosion resistance offered by the alloys on the basis of variation of corrosion resistance parameter.