CORROSION PROPERTIES OF NICKEL–FREE AUSTENITIC STAINLESS STEEL AS COMPARED WITH 18/8 STAINLESS STEEL

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The corrosion properties of a chromium-manganese-nitrogen austenitic stainless steel have been studied with respect to uniform corrosion, intergranular corrosion and pitting. In plain nitric acid, the rates were higher than 18/8 stainless steel. The kinetics were found to be of second order with respect to nitric acid concentration. Addition of sulphamic and sulphuric acids (0.3 M max) to 6N nitric acid has resulted in an increase in the corrosion rate of the steel. The test for intergranular corrosion in acidic copper sulphate solution showed that the nickel-free stainless steel corrodes at faster rate in the sensitized condition than 18/8 stainless steel. Similar results were also obtained in sulphuric acid + KCl indicating that the nickel-free stainless steel is more susceptible to pitting than 18/8 stainless steel. The latter results were confirmed by anodic polarization study also.

Several investigators[1–7] have reported the corrosion of various austenitic and martensitic stainless steels in nitric acid with and without addition of sulphuric acid. For processing of spent fuels from the nuclear reactors 347 SS is used as material of construction in 'Dissolvers' where 13 N nitric acid is used and in 'Evaporators' where concentration of the fission products is effected.

Research and Development work on substitute nickel-free austenitic stainless steels has been by done U.S. Steel Corporation, N.M.L.,[8] India and a few others. The substitutional aspects of stainless steels containing different amounts of chromium, manganese and nitrogen have been discussed by Nijhawan et al[8]. One of the reasons for their study is the shortage of nickel resources in the country. Nijhawan and co-workers[8] have reported that the corrosion resistance of the nickel-free steels is as good as 304 SS in boiling 65% nitric acid[9]. These steels could be used in the place of 18:8 Cr:Ni stainless steels for applications such as automobile and railway fittings, dairy equipments etc. and for special applications at high temperature by proper heat treatment. Systematic corrosion studies on this type of austenitic steel in nitric acid with addition of sulphamic and sulphuric acids have been reported in the present study and compared with those of conventional 304 SS reported elsewhere.

The effects of concentration of nitric acid have been studied. These results should be of interest to the nuclear chemical engineer in selection of material for an extraction process where the solvent nitric acid may contain additional constituents like sulphamic or sulphuric acids, uranyl nitrate etc.

In addition, in order to compare the susceptibility of this steel to intergranular corrosion and pitting corrosion, tests were carried out in the conventional Strauss solution (acidic copper sulphate) for intergranular corrosion and in 1N H_2SO_4 + 1N KCl solution for pitting. The results were compared with conventional austenitic stainless steel. The observations were supported by metallographic and electrochemical polarisation studies.

EXPERIMENTAL

The as-received (annealed) steel specimens of size 2 × 1.5 × 0.1cm (Cr 17.71%, Mn 17.55%, N 0.53%, C 0.08%, P 0.015%, S 0.019%, B 1 ppm) were degreased in benzene and acetone and then etched in 1 : 1 HCl for half a minute, washed in tap water, distilled water and acetone, and dried. The geometric surface area and the weight of the specimen were determined.

The corrosion test procedures were as reported earlier[1]. In brief, the apparatus consists of 1 litre concical flask fitted with a reflux condenser and a glass holder for the specimens. The 302 SS and nickel-free stainless steel specimens were examined for intergranular susceptibility in the sensitized condition at 650°C for ½ hour. The as-received specimens along with the sensitized specimens were subjected to Strauss test. Potentiostatic polarisation studies on the anodic behaviour of 302 SS and nickel-free stainless steel in 1 N H_2SO_4 and in 1 N H_2SO_4 + 1 N KCl were carried out at 28°C. Platinum was used as an auxiliary electrode and potentials were measured against saturated calomel electrode. The potentials were scanned at the rate of 20 mV per minute.

RESULTS AND DISCUSSION

1. Corrosion in nitric acid

In Fig. 1 the average rates of corrosion for this steel over a period of 10 days at various concentrations of nitric acid (6N to 12N) at 109°C are shown. The rate of corrosion at all concentrations is higher for nickel-free steel than the 302 SS and 321 SS[1]. The rate of corrosion is of second order with respect to concentration of nitric acid: $R = K.C^2_{HNO_3}$ where R = rate of corrosion in mm/year, K is a constant dependent on temperature. The corrosion rate values for nickel-free steel at all concentrations of nitric acid are unacceptably high. The acceptable values are <0.125 mm/year corresponding to <0.005 ipy as suggested by Uhlig[13]. The corresponding rates for 302 SS and 321 SS are within the acceptable values[1].

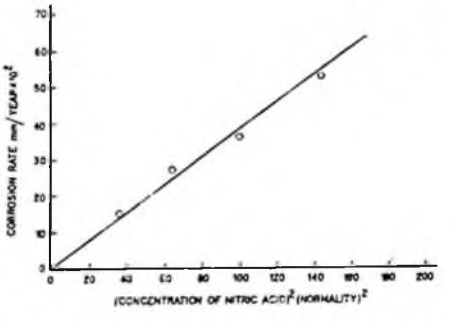


FIG. 1.-CORROSION RATES OF THACKERON STAINLESS STEEL IN NITRIC ACID AT 109°C VS (NORMALITY OF NITRIC ACID)²

These results show that the various types of austenitic stainless steels behave differently in nitric acid solution. This may be due to the different metallurgical phases and varied composition of the steel, though the heat treatment given is the same. It was observed that an essentially passive oxide layer was remaining on the surface of steel specimen throughout the test. As reported by Evans[10] and Glasstone[11], this complex oxide layer is not passive in the true sense of complete cessation of reaction but does bring down the rate of corrosion to a much lower value. The possible steps involved in the corrosion of stainless steel in nitric acid were discussed in earlier paper[1]. The fact that the passive complex oxide layer remains on the steel specimen throughout the test shows that the rate of formation of the oxide is greater than the rate of dissolution. Therefore, it is very likely that dissolution of this complex oxide layer on the surface of the specimen is the slowest and hence the rate-determining step. Jones[12] has observed that in dissolution of stainless steel in nitric acid, the amount of iron, chromium and nickel dissolved are approximately in the same proportion as they occur in the steel. The nature of the passive oxide layer with respect to dissolution should depend on the composition and metallurgical phases present in the steel specimen, and hence should lead to varying corrosion rates.

2. Effect of addition of sulphamic and sulphuric acids to 6N nitric acid

From Tables 1 and 2, it is seen that the corrosion rate in 6N nitric acid increases on addition of 0.1 M, 0.2 M, and 0.3 M sulphamic and sulphuric acids at the boiling temperature of 109°C. The plot of average weight (mg/dm²) against time in days in the case of addition of sulphamic acid was found to satisfy the relation $W = K.D^{1\cdot1}$ where W = weight loss (mg/dm²), D = time in days, K = rate constant. The K values when plotted against the concentration of sulphamic acid in molarity gave the relation $K = K'C^{0\cdot2}$, where K = rate constant, K' = another constant, C = concentration of sulphamic acid. Hence the kinetic equation $W = K.C^{0\cdot2}.D^{1\cdot1}$ was obtained for nitric acid-sulphamic acid mixtures.

TABLE 1 Effect of addition of sulphamic/sulphuric acids to 6N nitric acid at 109°C (B.Pt.) on the corrosion of nickel-free stainless steel

Conc of sulphamic/ sulphuric acids added to 6 N nitric acid	Average K values for		Equation for the amount of steel reacted (W) in relation to time in days and concentration for	
	Sulphamic acid	Suphuric acid	Sulphamic acid	Sulphuric acid
0.1 M	102.50	40 00		
0.2 M	117.50	87.50	$W = K'.C^{0\cdot2}.D^{1\cdot1}$	$W = K'C.D$
0.3 M	130.00	116.20		

TABLE—2 **Corrosion rates of stainless steels in HNO_3 with and without addition agents at 109°C B. Pt.**

Concentration of Solution	Corrosion rate (mm/year) on the basis of 10 days' test		
	302 SS	321 SS	Nickle-free SS
6N HNO_3	0.0321	0.0469	0.153
6N HNO_3 + 0.1 M $HSO_3.NH_2$	0.0500	0.0568	0.598
,, +0.2 M ,,	0.0626	0.0696	0.711
,, +0.3 M ,,	0.0765	0.0799	0.841
6N HNO_3 + 0.1 M H_2SO_4	0.0490	0 0433	0.197
,, +0.2 M ,,	0.0577	0.0512	0.398
,, +0.3 M ,,	0.0703	0.0590	0.526

Similarly, the effect of addition of 0.1 M, 0.2 M and 0.3 M sulphuric acid to 6N nitric acid at boiling temperature of 109°C gave the corresponding kinetic equation $W = K^1.C.D.$ Such relations for other steels have been reported earlier[2,3].

The higher corrosion rate of the steel obtained in the mixture of these acids viz. nitric+ sulphamic acids and nitric + sulphuric acids is probably due to the formation of sulphuric, hydrosulphamic and nitroxyl – sulphamic acids in the former and hydrosulphuric and nitroxylsulphuric acids in the latter respectively. These complexes add to some extent to the corrosion of the steel in nitric acid[3]. The passive complex oxide layer is observed on the steel specimen throughout the corrosion in these mixtures also.

3. Strauss test for intergranular susceptibility

The as-received specimens 302 SS and nickel-free steel along with the sensitized specimens have been subjected to Strauss test The results are shown in Table 3. It was found that the sensitized steel exhibited higher corrosion rate than the non-sensitized one. The nickel-free steel is found to be less resistant than the 302 SS in both the metallurgical conditions. The microstructures of non-sensitized and sensitized nickel-free steel are shown in Figs. 3 and 4 respectively. The sensitized steel shows the typical ditch structure at the grain boundaries and the non-sensitized one shows the typical austenitic structure. It is thus seen that the susceptibility of nickel-free steel to intergranular corrosion is also higher than that of 302 SS.

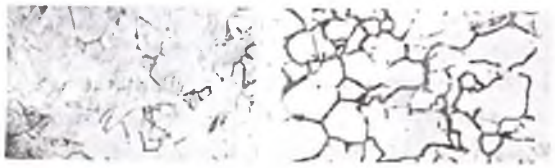


Fig. 3 As Received X200 Fig. 4 Sensitized X200

TABLE—3 **Strauss test for intergranular susceptibility**

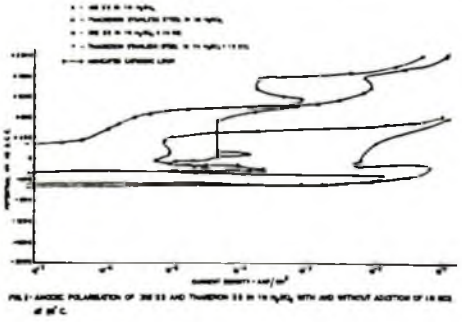
(47 ml of 98%H_2SO_4 + 13g. $CuSO_4.5H_2O$ per litre at 102°C)

Type of stainless steel	Mg/dm² in 72 hours	Corrosion rate mm/year	Observation from the photomicrograph
Annealed 302 SS	6.21	0.00961	
302 SS sensitized at 650°C for ½ hours	21.63	0.03349	Intergranular corrosion seen.
Annealed nickel-free stainless steel	20.29	0.03139	
Nickel-free stainless steel sensitized at 650°C for ½ hours	86.57	0.134	Intergranular corrosion seen

4. Test for pitting susceptibility

Pitting susceptibility of nickel-free steel by potentiostatic anodic polarisation studies were carried out for both the steels in 1N H_2SO_4 and also in 1N H_2SO_4 + 1N KCl at 28°C. The results are shown in Fig. 2. It is seen that in pure 1N H_2SO_4, 302

SS is already passive (the open circuit potential being + 300 mV vs SCE), while the nickel-free steel is active (the open circuit potential being -560 mV vs SCE) and shows an active-passive transition with a cathodic loop when anodically polarised. The occurrence of cathodic loop indicates the co-existence of active and passive condition at open circuit. Similar cathodic loop has been reported for 304 SS[14].



In the presence of 1N KCl the passive range in both cases gets reduced. The 302 SS has become active and shows an active-passive transition, with passivity breakdown at about +300mV. The nickel-free steel shows an extremely high critical current in the presence of 1N KCl (7×10^{-2}amp/cm^2), very narrow passive range and an active breakdown potential (—100 mV vs SCE). Both the steels after anodic polarisation showed pitting. The above results indicate that the nickel-free steel is less passive in 1N H_2SO_4 and is more susceptible to pitting in chloride-containing solutions (Table 4).

TABLE—4 **Corrosion rates of stainless steels at 28° in H_2SO_4 + KCl solutions for 1 day exposure**

Type of stainless steel	Conc of solution	Corrosion rate mm/year	observation
Nickel-free stainless steel	1 N H_2SO_4	nil	Pitting was observed in cloride containing solutions.
"	1 N H_2SO_4 + 1N KCl	5.34	
302 SS	1 N H_2SO_4	nil	
"	1 N H_2SO_4 + 1N KCl	0.481	

Apparently, the presence of manganese gives rise to a defective structure in the passive oxide which is easily removed by the agressive chloride ion. The presence of nickel in 302 SS is probably not leading to a very defective structure in the passive oxide. The occurrence of such defective structures and the role of manganese have to be confirmed by future studies.

CONCLUSIONS

1. The corrosion rate of a chromium-manganese-nitrogen stainless steel in nitric acid is higher than 302 SS and 321 SS and is of the second order with respect to the normality of the acid.

2. The individual effects of sulphamic and sulphuric acids to boiling 6N nitric acid show that the rate of corrosion is higher than in plain boiling 6N nitric acid. The effect is, however, lower with the addition of sulphuric acid than sulphamic acid.

3. The rate of formation of the passive complex layer on the steel is greater than the rate of dissolution of this layer in nitric acid and in the presence of small amounts of sulphamic and sulphuric acids.

4. The chromium-manganese-nitrogen steel is more susceptible than the austenitic steels with respect to intergranular corrosion in acidic copper sulphate solution and to pitting in H_2SO_4 + KCl solutions.

5. In general, the chromium-manganese-nitrogen steel is less corrosion resistant than chromium-nickel austenitic steels.

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REFERENCES

1. P.R. Shibad, J. Balachandra and P.K. Jena, Indian Journal of Applied Chemistry, 30(3–4) (1967) 69
2. P.R. Shibad, P. K. Jena and J. Balachandra ibid, 33–1(1970) 25
3. P. R. Shibad, J. Balachandra and P. K. Jena, ibid. 33–3 (1970) 159
4. P.R. Shibad, P.K. Jena and J. Balachandra ibid, 34–3 (1971) 118
5. P.R. Krystow and M. Balicki, Corrosion, 12, (1956) 39
6. Hatfield, "Stainless Iron and Steel", by J.H.G. Monypenny, Chapman and Hall Ltd., London (1951)
7. McKinnel (Jr), M.G. Fontana, L.F. Lockwood, R. Speiser and P.H. Beck, Corrosion, 14 (1956) 27
8. B.R. Nijhawan, P. K. Gupta, S. S. Bhatnagar, B.K. Guha and S.S. Dhanjal, Symp 'on 'Metallurgy substitute ferrous and non-ferrous alloys' Jamshedpur, April, 1966
9. Russel Franks, The Corrosion Handbook, edited by H.H. Uhlig, John Wiley and Sons Inc. (1955) p. 185
10. U. R. Evans, "Th Corrosion and oxidation of metals" Edward Arnold Publisher, London (1961) p. 328
11. S. Glasstone, "Text-book of physical chemistry" (1940) p 1011
12. H.N. Jones, Research and Development Branch, Culcheth Laboratories, United Kingdom Atomic Energy Authority, p.5 RDB (C)—TN—16 (1958)
13. H.H. Uhlig, Corrosion & Corrosion Control, John Wiley and Sons Inc. (1971) p. 14
14. K. Elayaperumal, P.K. De and J. Balachandra. Corrosion, 28 (1972) 270

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