Corrosion Behaviour of Low Carbon Austenitic Stainless Steels in Mineral Acids

P. R. SHIBAD AND K. N. ADHE
Metallurgy Division, Bhabha Atomic Research Centre
Trombay, Bombay-400 085

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THE corrosion behaviour of SS 304 L and SS 316 L has been compared with respect to uniform corrosion, intergranular corrosion and pitting. The media chosen were plain nitric acid, nitric acid with addition of sulphuric acid, acidic copper sulphate and sulphuric acid and with KCl additions. In plain HNO_3, the corrosion rates of SS 316 L were of a higher order than SS 304L. The kinetics were found to be of first and second order for SS 304 L and SS 316 L respectively with respect to HNO_3 concentration.

Addition of 0.4 M H_2SO_4 to 6 N HNO_3 has resulted in an increase in the corrosion rate of the steels. The test for intergrannular corrosion carried out in acidic copper sulphate solution showed that SS 316 L corrodes at a faster rate than SS 304 L which was confirmed by microstructural examination. However, in plain H_2SO_4, higher corrosion rates were seen for SS 304 L as against SS 316 L. Pitting was not observed in 1 N $H2SO_4$ + 1 N KCl, and higher current densities were found for SS 304 L than SS 316 L which were confirmed by anodic polarisation studies.

A NUMBER of investigations have been carried out to study the nature of corrosion of various types of stainless steel in nitric acid[1-8]. For processing of spent fuels from the nuclear reactors, Type 347 SS is generally used as material of construction in 'Dissolvers' and 'Evaporators' where about 13 N HNO_3 is being used. Currently Type 304 L SS is an important material for this application. This material has also been chosen frequently for Purex plant equipment. In a survey on corrosion of various types of stainless steel in solutions containing nitric acid, the effects of sensitization and weldments on corrosion penetration and evaluations of corrosion rates at different temperatures and evaluations of corrosion rates at different temperatures and acid concentrations have been snmmarized. In thls connection, a study on Type 316 L SS is of interest for their corrosion behaviour in HNO_3.

In the present work, corrosion of SS 304 L and SS 316 L has been studied in HNO_3 at various concentrations and temperetures with and without the addition of small quantities of H_2SO_4. Studies have also been carried out in 1 N H_2SO_4 with and without the addition of 1 N KCl for pitting. Potentiostatic polarisation on the anodic behaviour of these steels in the latter solutions have been made. Strauss test for intergranular susceptibility has been carried out after a suitable sensitizing treatment.

EXPERIMENTAL

The as-received (annealed) SS 304 L and SS 316 L specimens of size $2 \times 1.5 \times 0.3$ cm^3 having the composition C 0.02%, Cr 18.62%, Ni 10.19% and C 0.03%, Cr 18%, Ni 10%, Mo 1.75% respectively were degreasad in acetone and benzene and then etched in 1 : 1 HCl for half a minute. The specimens were thoroughly washed successively in tap water and distilled water, degreased in acetone and finally dried. The weights of the specimens were determined using a semi-micro saratorius balance. All the acids used were of chemically pure grade.

The corrosion test procedures were the same as those reported in an earlier work[1]. In brief, the apparatus consists of 1 litre conical flask fitted with a reflux condenser and a glass holder for the specimens. The SS 304 L and SS 316 L specimens were examined for intergranular suspectibility after treating at 650°C for 1 day. The as-received specimens along with the sensitized specimens were subjected to Strauss test. Potentiostatic polarization studies on the anodic behaviour of these steels both (as-received and sensitized) 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. The potentials were scanned at the rate of 20 mV/minute.

RESULTS

1. *Corrosion in nitric acid :* Table 1 summarises the average corrosion rates for these steels over a period of 2 days at various concentrotions of nitric acid (6 N to 12 N) and at various temperatures.

TABLE 1

Effect of temperature and concentration on the corrosion rates of low carbon stainless steels

Concentration of HNO_3	Temperature °C	Corrosion rate (mdd) based on 2 days' test for SS 304L	Corrosion rate (mdd) based on 2 days' test for SS 316L	Remarks
	90	10.6	12.1	Dark blackish passive complex oxide layer is seen on the specimens after corrosion in HNO_3 solutions at the concentrations and temperatures reported; Order of reaction is found to be 1 and 2 for SS 304L and SS 316L respectively.
	100	18.3	22.6	
10 N	104	21.4	33.8	
	109	24.0	39.8	
	116	53.6	89.1	
6 N		14.1	15.4	
8 N		19.7	21.3	
10 N	109	24.0	39.7	
12 N		31.3	55.7	

a) The corrosion rates for SS 340 L are lower than SS 316 L at all concentrations and temperatures of HNO_3. These values for SS 304 L and SS 316 L are acceptable upto 10 N HNO_3 and 8 N HNO_3 at 109°C respectively (<5 mpy).

b) The rate of corrosion is of first and second order with respect to concentration of nitric acid for SS 304 L and SS 316 L respectively i.e. $R = K.C_{HNO3}$ for SS 340 L and $R = KC^2_{HNO3}$ for SS 316 L, where R = rate of corrosion in mdd and K is a constant dependent on temperature.

2. *Effect of addition of 0.4 M H_2SO_4 to 6 N HNO_3 :* The results on corrosion of these stainless steels in plain boiling 0.4 M H_2SO_4 and a mixture of H_2SO_4 and HNO_3 are summarized in Table 2. There was no passive layer formation on the surface in plain 0.4 M H_2SO_4 medium. Very high corrosion rates have been observed for SS 304 L and SS 316 L, however SS 304 L has shown greater dissolution in this medium. In presence of boiling 6 N HNO_3 + 0.4 M H_2SO_4 solution, the rates have decreased to 37.1 and 38.1 mdd respectively, for SS 304 L and SS 316L. These rates are still in the higher range. The presence of HNO_3 added to H_2SO_4 inhibits the dissolution rate to a great extent ; but these rates are still not within the acceptable range of <5 mpy.

3. *Strauss test for intergranular susceptibility :* The as received SS 304 L and SS 316 L specimens along with the sensitized specimen (at 650°C for 1 day followed by furnace cooling) have been subjected to Strauss test. The results are shown in Table 3. It was found that the sensitized eteels exhibited higher corrosion rates than the as-received ones. The SS 304 L exhibits lower corrosion rates than SS 316 L both for as-received and sensitized specimens. The microstructures of these specimens are shown in Figs. 1-4. Figs. 1 and 3 show the typical austenitic structure for SS 304 L and SS 316 L respectively. The SS 304 L does not exhibit any intergranular attack as is evident from Fig. 2. Fig. 4 shows the typical ditch structure at the grain boundaries for SS 316 L.

TABLE 2

Corrosion rates of stainless steel in boiling 6 N HNO_3 with addition of 0.4 M H_2SO_4 solution (B.Pt. 109°C)

Concentration of solution	Corrosion rate (mdd) based on 1 days' test for SS 304L	Corrosion rate (mdd) based on 1 days' test for SS 316L	Remarks
0.4 M H_2SO_4	36,357 (6543)*	1792 (322.2)*	No passive layer seen after corrosion
6 N HNO_3 + 0.4 M H_2SO_4	37.14 (6.68)*	38.11 (6.85)*	Passive complex oxide seen after corrosion

*mpy values

TABLE 3

Strauss test for intergranular susceptibility (47 ml of 98% H_2SO_4 + 13g. $CuSO_4$ $5H_2O$ per litre, boiling at 103°C

Type of stainless steel	Corrosion rate (mpy) on the basis of 72 hrs' test for		Observation from photomicrograph
	SS 304L	SS 316L	
Annealed steel	0 54	0.81	No intergranular corrosion
Sensitized steel at 650°C for 1 day	1 89	7.63	Intergranular corrosion seen only for SS 316L



FIG. 1 'As-received' SS 304 L(×200)

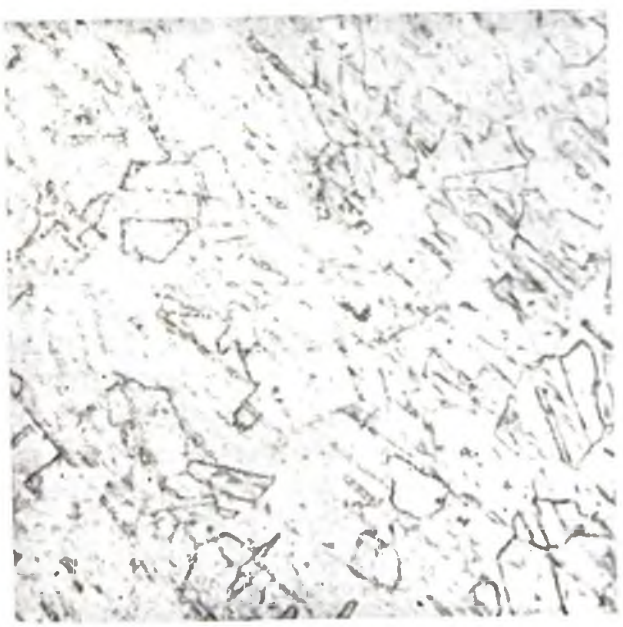


FIG. 2 Sensitized SS 304 L(×200)



FIG. 3 As-received' SS 316 L(×130)

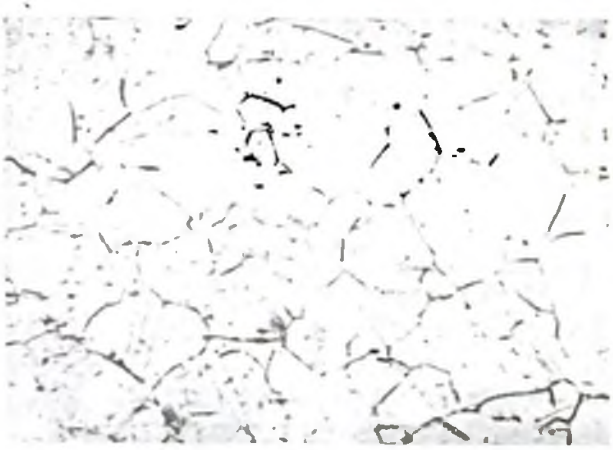


FIG 4 Sensitized SS 316 L(×130)

4, *Test for pitting susceptibility :* The corrosion rates on these two steels have been carried out at 28°C in 1 N H_2SO_4 and in 1 N H_2SO_4 + 1 N KCl over an exposure peried for 2 days. The results are shown in Table IV. Both these steels show that the presence of 1 N KCl increases the corrosion rates considerably. Pitting is not observed in both these steels after corrosion in these solution.

TABLE 4

Corrosion rates of stainless steels in N H_2SO_4 + 1 N KCl solution on the basis of 2 days' tsst at 28°C

Types of stainless steel	Concentration of solution	Corrosion rate mdd	Observation after corrosion
SS 304 L	1 N H_2SO_4	201.7 (36.0)*	No pitting observed
	1 N H_2SO_4 + 1 N KCl	981.1 (176.5)*	-do-
SS 316 L	1 N H_2SO_4	2.7 (0.50)*	-do-
	1 N H_2SO_4	131.1 (23.3)	-do-

*mpy values

Potentiostatic anodic polarisation studies were carried out for these steels in as-received and sensitized condition in 1 N H_2SO_4 and in 1N H_2SO_4 + 1 N KCl at 28°C. The polarisation characteristics are shown in Table V and Figs. 5 and 6. For SS 304 L and SS 316 L, the corrosion potentials of + 32 and + 140 mV indicate that these are in passive region, and that SS 316 L has better passive properties. On adding 1 N KCl to the medium, the shift in the corrosion potentials to negative values indicate that the alloys are in the active region (dissolution). Considerable dissolution of these alloys have been observed (Table 4). After heat treatment at 65°C for 1 day, the potentials have been shifted to active region again.

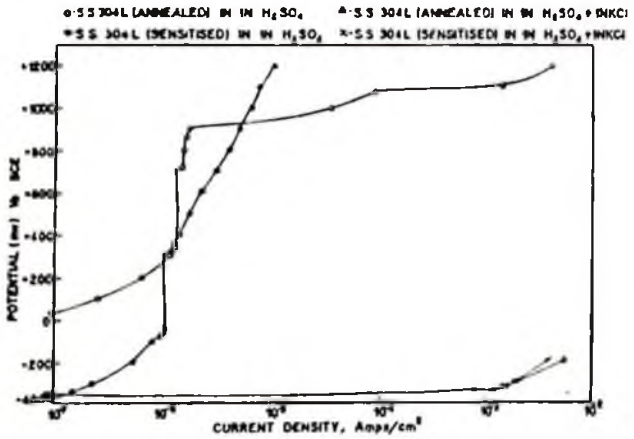


FIG 5 ANODIC POLARISATION OF S.S 304L (ANNEALED AND SENSITISED) IN IN H_2SO_4 WITH AND WITHOUT 1N KCl AT 28°C

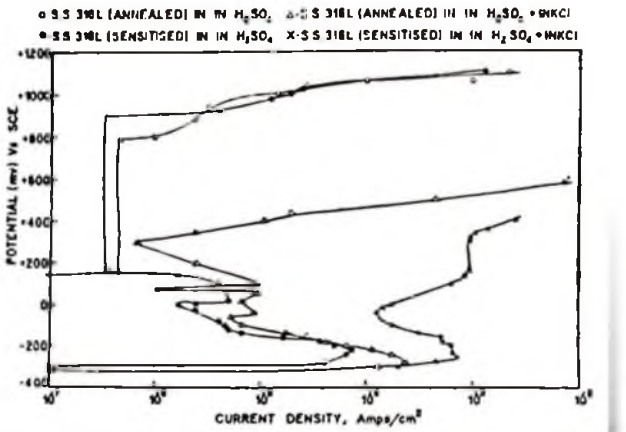


FIG 6 ANODIC POLARISATION OF S.S 316 L (ANNEALED AND SENSITISED) IN IN H_2SO_4 WITH AND WITHOUT ADDITION OF 1NKCl AT 28°C

In plain 1 N H_2SO_4, the as-received SS 304 L exhibits a passive current density of about 5×10^{-6} amp/cm² with a passive range of 600 mV. In the same medium the sensitized specimen also

TABLE 5

Anodic polarisation characteristics of stainless steels in 1 N H_2SO_4 and in 1 H_2SO_4 + 1 N KCl at 28°C

Types of stainless steel	Concentration of solution	Corrosion vs SCE mv	Passive current density amp/dm2	Passive range mv
Annealed SS 304 L	1 N H_2SO_4	+ 32	5×10^{-6}	600
-do-	1 N H_2SO_4 + 1 N KCl	- 350	—	—
Sensitized SS 304 L	1 N H_2SO_4	- 370	1×10^{-6}	340
-do-	1 N H_2SO_4 + 1 N KCl	- 350	—	—
Annealed SS 316 L	1 N H_2SO_4	+ 140	4×10^{-7}	620
-do-	1 N H_2SO_4 + 1 N KCl	- 320	—	—
Sensitized SS 316 L	1 N H_2SO_4	- 300	3.4×10^{-7}	750
-do-	1 N H_2SO_4 + 1 N KCl	- 320	—	—

exhibits passivity with a current density of 1×10^{-6} amp/cm^2, but having a passive range of only about 240 mV.

In the case of SS 316 L (as-received), clear passivity is observed with a passive range of 620 mV and a current density of 4×10^{-7} amp/cm^2. The sensitized specimen shows fluctuations in the currents initially, and the passivity is attained after a potential of + 150 mV.

In the presence of 1 N KCl in 1 N H_2SO_4, these steels both in the as received and sensitized conditions exhibit simple anodic dissolution and do not exhibit passivity. In general, it has been observed that SS 304L exhibits higher anodic current densities than SS 316L. It is thus seen that passive current densities for SS 304L are found to be much higher than those obtained for SS 316L with and without the presence of 1 N KCl.

DISCUSSION

1. *Corrosion in nitric acid:* The corrosion rates for SS 304L are higher than SS 302, SS 310 SS 321 and SS 347 in HNO_3. It is interesting to note that while SS 304 has higher corrosion rates than SS 304L, reverse is the case observed for SS 316 and SS 316L. The acceptable values of corrosion rate viz., <5 mpy for uniform corrosion is valid for SS 304 in 6 N HNO_3 at 109°C (B.Pt) while for SS 316 they do not satisfy this range[1]. It has been found that the various types of stainless steels behave differently in HNO_3 solutions. This may be due to the different metallurgical phases and varied compositions of the steel, though the heat treatment given to all these steels is the same before corrosion. It was observed that a passive complex oxide layer was remaining on the surface of steel specimen throughout the test. The various steps involved in the corrosion of stainless steels in HNO_3 have been discussed in earlier papers [1,10,11].

2. *Effect of addition of 0.4 M H_2SO_4 to 6 N HNO_3:* In boiling 0.4 M H_2SO_4, SS 304L and SS 316 L exhibit higher corrosion rates than SS 304 and SS 316 respectively. SS 304 L is found to have higher corrosion rates than SS 302, SS 309, SS 310, SS 321, SS 347 and SS 414 while SS 316 L exhibits higher corrosion rates than SS 321 and SS 321 and 347[2] amongst the above-mentioned steels. In the case of all these steels studied earlier[2] and presently, addition of 6 N HNO_3 to 0.4 M H_2SO_4 reduces the corrosion rate i.e. HNO_3 acts as an passivator and maintains the passive film throughout the corrosion process.

3. *Pitting and anodic polarisation:* As observed in the case of the low carbon stainless steels (304 and 316), earlier work has shown[12] that the presence of 1 N KCl in 1 N H_2SO_4 increases the corrosion rates of SS 302 and 'Thackeron' stainless steel. However, pitting was observed for the latter steels in chloride containing solution unlike for the low carbon stainless steels. These steels exhibit such higher corrosion rates, both in 1 N H_2SO_4 and 1 H_2SO_4 + 1 N KCl solutions, than SS 302 and 'Thackeron' stainless steel. The low carbon stainless steels are found to have better passivation characteristics than 'Thackeron' stainless steel and SS 302[12], though the dissolution rates for low carbon stainless steels are much higher. However, pitting was not observed for the latter steels in 1 N H_2SO_4 + 1 N KCl unlike SS 302 and 'Thackeron' stainless steel. This shows that the dissolution of low carbon stainless steel is of a uniform type of corrosion even in presence of chlorides in 1 N H_2SO_4.

CONCLUSIONS

1. The SS 304 L is better corrosion resistant than SS 316 L in HNO_3 solutions of concentrations 6 N-12 N and at temperatures studied.

2. The corrosion rates of SS 304 L and SS 316 L in HNO_3 are found to be of first and second order w.r.t. the normality of the acid.

3. The corrosion rates for these steels in boiling 0.4 M H_2SO_4 are considerably reduced in presence of 6 N HNO_3. A passive complex oxide is seen after corrosion in boiling 6 N HNO_3 and in boiling 6 N HNO_3 + 0.4 M H_2SO_4. The SS 316 L exhibits better corrosion resistance than SS 304 L in both these solutions.

4. Strauss test reveal that SS 304 L is better corrosion resistant than SS 316 L, which is confirmed by microstructural examination in that SS 316 L exhibits ditch type structure showing intergranular corrosion.

5. SS 316 L exhibits better corrosion behaviour than SS 304 L both in 1 N H_2SO_4 and in

1 N H_2SO_4 + 1 N KCl. Pitting is not observed in these steels after corrosion, which is confirmed by anodic polarisation studies.

6. SS 304 L is good material for nitric acid service.

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