Corrosion and inhibition of aged 347 grade stainless steel boiler tubes

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General and pitting corrosion of both service and laboratory aged 347 grade stainless steel superheater tubes have been investigated. SEM analysis showed the precipitate phases to have a double structure consisting of σ phase and carbide. EDA analysis of the precipitates indicated the [Cr]/[Fe] ratio to increase with exposure time. For both set of specimens, the general corrosion rate in 1 M H_2SO_4 increased with aging whilst the pitting studies (in 3.5% NaCl) also indicated increased pitting susceptibility with aging. These trends are consistent with corrosion from the chromium depleted areas adjacent to the precipitates. Methoxypropylamine is effective as an inhibitor for pitting corrosion and the concentration required to prevent this form of attack increases with exposure time for both types of specimens.

1. Introduction

Minami *et al.* [1] have shown that when 347 grade stainless steel (SS) is heated niobium and chromium type carbides form in addition to the hard, brittle, intermetallic σ phase. This alloy is used for superheater (S/H) tubes in fossil-fuel fired power stations and during their service life (up to 100 000 h or more) the inner walls of the tubes are exposed to corrosive environments containing a range of impurities [2] and this may give rise to pitting corrosion. While the detrimental effect of σ phase on the corrosion behaviour of austenitic SS has received attention [3–5] little work appears to have been done on the effect of inhibitors such as amines on the pitting corrosion of aged alloys. In the present paper, the general and pitting corrosion characteristics of both service and artificially aged 347 grade SS have been examined. In addition the inhibiting action of methoxypropylamine (MPA) for pitting corrosion has been studied.

2. Experimental details

2.1. Materials and reagents

Specimens were cut from 347 grade SS S/H tubes which had been exposed at approx. 650° C in a S.E. Queensland power station for 59 710, 92 823 and 98 000 h, respectively. The mean chemical composition of this alloy was as follows: Fe: 68.62%; Cr: 18.31%; Ni: 11.56%; Nb: 0.70%; S: 0.10% and Si: 0.70%. Specimens cut from a new (as received) tube were also laboratory aged in a muffle furnace in air at 800° C for set periods (800, 2000 and 4000 h). Additionally a specimen cut from a piece of new tube was

annealed in air at 1050° C for 2 h and then water quenched (to dissolve any σ phase present).

1 M H_2SO_4 was used for the general corrosion studies and the pitting corrosion resistance was evaluated in 3.5% (w/w) NaCl. 3.5% NaCl solution containing different concentrations of methoxypropylamine (MPA) (marketed as PRE-TECT 2000; product manufactured by Hach Chemicals Co., USA) was used for the inhibition experiments while a 10 M KOH solution was employed as etchant to identify precipitate phases. All reagents were AR grade (except the MPA) and all solutions were prepared from distilled deionized water.

2.2. Electrochemical measurements

Specimens ($\sim$ 1 cm^2) were mounted in chemical resistant epoxy resin to form the working electrode (WE). A platinum counter electrode (CE) was mounted similarly to the WE and a saturated calomel electrode (SCE) fitted with a Luggin capillary was used as reference. The cell was as previously described [6] and was suspended in a temperature controlled water bath ($25 \pm 1°$ C). Polarization curves were recorded using a Wenking LB75L potentiostat interfaced to an IBM compatible personal computer [7].

The WE was polished using a 1200 grade SiC paper and was then washed and degreased in AR grade acetone before use. Immediately after polishing the WE was placed in nitrogen purged (1 h) 1 M H_2SO_4 and prepolarized at -1000 mV vs SCE for 10 min. The corrosion potential (E_{corr}) was then recorded and after stabilization (up to 1 h) polarization was commenced. The potential was scanned from $E_{corr} - 200$ mV at 30 mV min^{-1} to a predefined maximum potential of $+1200$ mV.

For measurements of the pitting potential (E_{pit}) in 3.5% NaCl (pH 6.6) the procedure adopted was

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Table 1. Analysis and polarization data for both service and laboratory aged 347 grade SS S/H tubes in nitrogen purged 1 M H_2SO_4 at 25° C

Exposure time/h	[Cr]/[Fe] ratio	E_{corr} /mV	i_{crit} /A cm^{-2}	i_{cp} /A cm^{-2}	A /A cm^{-2} mV	%IC
59710 (sa)	0.53	−401	1.1×10^{-2}	3.7×10^{-6}	0.7914	2214
92823 (sa)	0.63	−399	1.3×10^{-2}	1.4×10^{-5}	0.9233	2600
98000 (sa)	0.66	−394	1.5×10^{-2}	3.3×10^{-5}	1.1052	3132
0 (an)	−	−410	1.9×10^{-4}	3.4×10^{-6}	0.0342	0
0 (ar)	0.27	−413	1.4×10^{-3}	3.5×10^{-6}	0.0730	113.5
800 (la)	0.31	−401	2.0×10^{-3}	2.2×10^{-5}	0.1531	347.7
2000 (la)	0.35	−397	5.4×10^{-3}	3.5×10^{-5}	0.2445	614.9
4000 (la)	0.40	−392	6.1×10^{-3}	4.1×10^{-5}	0.2983	772.2

sa = service aged; an = annealed; ar = as received; la = laboratory aged.

as above up to and including the realization of E_{corr} ($\sim$ 2 h). The WE was then polarized in the positive direction from E_{corr} at 30 mV min^{-1} to a potential where a permanent increase in current density was observed (10^{-3} A cm^{-2}). The same procedure was followed for specimens immersed in the 3.5% NaCl solution containing different concentrations of MPA (3.5×10^2 p.p.m. to 3.0×10^3 p.p.m.).

All polarization runs were done at least in duplicate.

2.3. Metallography

Specimens were polished to a mirror finish with 1 μm diamond paste and then etched electrochemically in 10 M KOH using a 3 V dry cell for 5 s to identify the precipitate phases [8]. Energy dispersive analysis (EDA) using a Jeol JXA-840A scanning electron microscope (SEM) was used to determine the composition of the precipitates. At least 10 precipitate zones were analyzed (10 positions within each zone) and the results were averaged. The 'background' concentrations for chromium and iron were determined similarly on regions well removed from the precipitates and also using the specimen cut from a new tube.

3. Results and discussion

3.1. Microstructural analysis of precipitate phases

Precipitate phases were revealed in both types of aged specimens but not for the 'as received' specimen. In a previous paper [8] it was shown that precipitate phases in service aged 347 grade SS specimens had a double structure consisting of σ phase and carbides. The mean [Cr]/[Fe] ratio for precipitate phases in the specimens together with the expected background ratio for the alloy (approx. 0.27) is shown in Table 1. A linear relationship has been shown to exist between the [Cr]/[Fe] ratio and aging time for both types of specimen [8] and an increasing [Cr]/[Fe] ratio for precipitate phases also reflects increased chromium depletion in areas adjacent to the precipitates. In addition, data from the work of Saito et al. [9], shows a direct relationship between this ratio and the creep damage ratio for service aged 316 grade SS S/H tubes. The [Cr]/[Fe] ratio has therefore been proposed as a measure of alloy degradation.

3.2. General corrosion

Typical polarization curves for service aged and for the 'as received' and annealed specimens in nitrogen purged 1 M H_2SO_4 are shown in Fig. 1. Curves were similar for the laboratory aged specimens. In each case an active/passive transition was observed. During prepolarization at −1000 mV vigorous hydrogen evolution probably exposes the alloy in those regions where the passive film is thin and less protective, i.e. zones adjacent to the chromium precipitates. Subsequent anodic polarization in acid results in metal dissolution from the chromium depleted zones and this is followed by passivation and then oxygen evolution at potentials more positive than +750 mV.

An estimate of the general corrosion experienced by a specimen can be obtained by determining the amount of charge passed during anodic polarization, for example from E_{corr} to some predetermined potential. In the present case current density (A cm^{-2}) was plotted against potential (mV) (E_{corr} to E_{corr} + 300 mV) and the area (A) under the curve was used as a measure of the charge passed. The
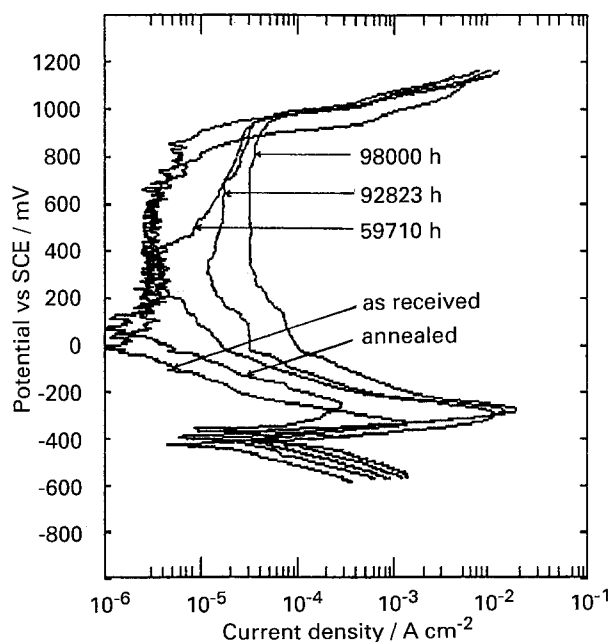

Fig. 1. Typical potentiodynamic polarization curves for annealed, 'as received' and service aged 347 grade SS S/H tubes in nitrogen purged 1 M H_2SO_4 (30 mV min^{-1}; 25° C).

percentage increase in corrosion rate (%IC) with aging was also calculated using the following expression

$$\%IC = \frac{\{A_a - A_{an}\}}{A_{an}} \times 100$$

where A_a is the area for the aged specimen, and A_{an} the area for the annealed specimen.

For each type of specimen, corrosion is seen to increase with aging time (Table 1), i.e. as the amount of chromium in zones adjacent to the precipitates decreases. This trend is similar to that reported by Potgieter [3] for SAF 2205 duplex stainless steel. It can also be seen from Table 1 that annealing has the effect of decreasing general corrosion (although no precipitates were observed in the 'as received' and

Table 2. Polarization data for both service and laboratory aged 347 grade SS S/H tubes in nitrogen purged 3.5% NaCl solution at 25° C, pH 6.6

Exposure time/h	E_{corr} /mV	E_{pit} /mV	$\mid E_{pit} - E_{corr} \mid$ /mV	i_{cp} /A cm^{-2}
59710 (sa)	−540	−51	489	6.0×10^{-6}
92823 (sa)	−581	−104	477	8.3×10^{-6}
98000 (sa)	−603	−115	448	1.2×10^{-5}
0 (an)	−500	230	730	3.5×10^{-6}
0 (ar)	−494	122	616	4.7×10^{-6}
800 (la)	−585	−190	395	5.2×10^{-6}
2000 (la)	−610	−300	310	8.8×10^{-6}
4000 (la)	−645	−346	299	1.9×10^{-5}

sa = service aged; an = annealed; ar = as received; la = laboratory aged.

annealed specimens). In addition the general corrosion is more pronounced in the service aged specimens and this is probably due to the higher [Cr]/[Fe] ratios compared to those obtained for laboratory aged specimens. The observed active/passive transition reflects the formation of a film on chromium depleted zones and reference to Fig. 1 shows that the passive film in these regions becomes less protective the longer the aging time of the alloy (i.e. i_{cp} increases). This behaviour was also exhibited by the laboratory aged specimens and is not dissimilar to that observed for the polarization of alloys with nickel contents of 8.3 to 9.8% and variable chromium contents (3.5 to 19.2%) in hot 4 M H_2SO_4 [10]. Here i_{cp} increased with decreasing chromium concentration. The critical current density (i_{crit}) is also seen to increase with aging and this was comparable to studies by Osozawa *et al.* on 304 grade SS [11].

3.3. Pitting corrosion

Typical anodic curves for service and laboratory aged specimens polarized in nitrogen purged 3.5% NaCl are presented in Fig. 2(a) and (b), respectively. The
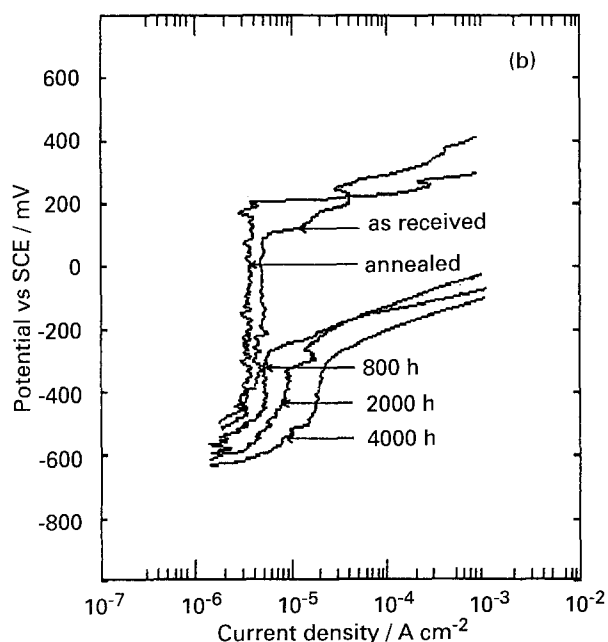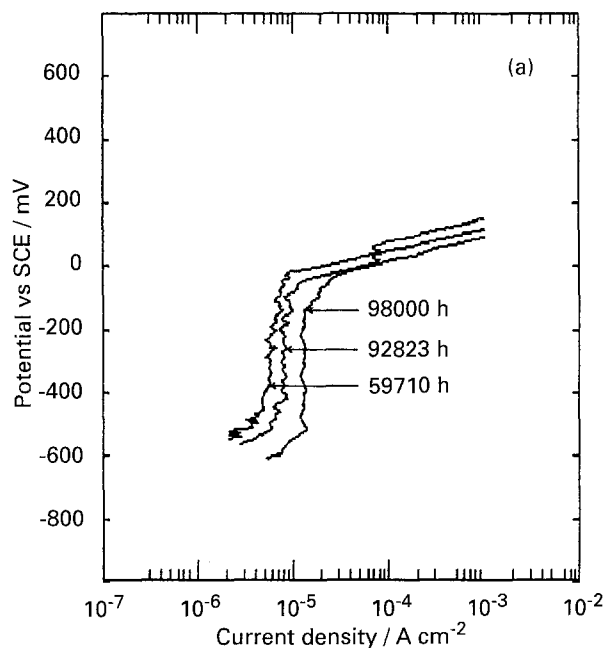
Fig. 2. Typical potentiodynamic anodic polarization curves for (a) service aged and (b) laboratory aged 347 grade SS S/H tubes in nitrogen purged 3.5% NaCl solution (30 mV min^{-1}; 25° C; pH 6.6).
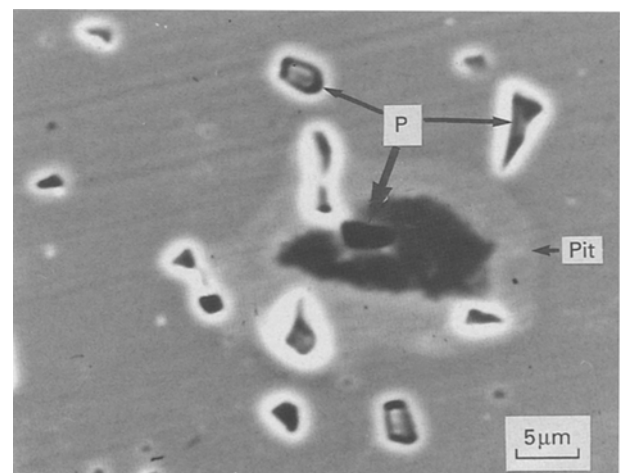
Fig. 3. Micrograph of service aged (98 000 h) 347 grade SS S/H tube showing precipitates (marked P) and a pit after polarization in 3.5% NaCl, polishing and electrochemical etching.

Table 3. Polarization data for both service and laboratory aged 347 grade SS S/H tubes in nitrogen purged 3.5% NaCl solution + 700 p.p.m. MPA (25° C, pH 10.7)

Exposure time/h	E_{corr} /mV	E_{pit} /mV	$\|E_{pit} - E_{corr}\|$ /mV	i_{cp} /A cm^{-2}
59710 (sa)	−566	70	636	4.9×10^{-6}
92823 (sa)	−597	30	627	4.7×10^{-6}
98000 (sa)	−649	15	664	6.4×10^{-6}
0 (an)	−530	300	880	3.0×10^{-6}
0 (ar)	−517	208	725	3.4×10^{-6}
800 (la)	−636	−112	524	3.9×10^{-6}
2000 (la)	−664	−154	510	8.3×10^{-6}
4000 (la)	−670	−190	480	1.2×10^{-5}

sa = service aged; an = annealed; ar = as received; la = laboratory aged.

cathodic reaction is now reduction of water [12] and this leads to E_{corr} being more negative than for corrosion in 1 M H_2SO_4. In addition the higher pH (6.6) results in the active/passive transition being less pronounced. The mean polarization data is presented in Table 2. As in acid, i_{cp} increased with aging. The pitting potential and E_{corr} are also observed to shift in the negative direction with increased exposure time and if the absolute difference between E_{pit} and E_{corr}, i.e. $|E_{pit} - E_{corr}|$ is taken as a measure of the pitting resistance of the alloy [13] this is also seen to decrease with aging.

The inferior pitting corrosion resistance of the aged specimens can also be attributed to the formation of increasingly chromium rich precipitate phases with the depletion of chromium in the adjacent matrix providing favourable sites for pit initiation [5]. An

SEM micrograph of a service aged specimen (98 000 h) after polarization in 3.5% NaCl followed by polishing with 1 μm diamond paste and electrochemical etching is shown in Fig. 3. Precipitates are marked (P) and it can be seen that a pit tends to form in a region adjacent to the precipitate. No pits were observed in the matrix removed from precipitates. As in the case of general corrosion annealing increases the pitting resistance of the alloy. It would also be expected that laboratory aged specimens, with a relatively low [Cr]/[Fe] ratio compared to that for service aged specimens, should show superior pitting corrosion resistance. The results in Table 2, however, show that the opposite is the case and this may be due to the formation of different types of precipitates which provide more susceptible pit initiation sites. For example, when the exposure time is increased carbides initially formed coarsen and this is followed by σ phase formation [1].

The effect of 700 p.p.m. MPA on the pitting characteristics of each of the specimens in 3.5% NaCl solution was investigated and the results are presented in Table 3. The data reveals that the addition of inhibitor rendered E_{corr} more negative and this can be attributed to the increase in pH from 6.6 to 10.7 on the addition of 700 p.p.m. amine. Addition of MPA also shifted E_{pit} to more positive potentials and prompted formation of a more protective film (i_{cp} decreases for each specimen). The inhibitor, therefore, has the effect of increasing the passive range (i.e. $|E_{pit} - E_{corr}|$) making each sample less susceptible to pitting attack. The trend observed in Table 2 for E_{corr}, E_{pit} and i_{cp} with aging in general was retained in the presence of the inhibitor.

Further experiments were carried out to examine the effect of inhibitor concentration on the pitting

Table 4. Polarization data for 'as received' and service aged 347 grade SS S/H tubes in nitrogen purged 3.5% NaCl containing different concentrations of MPA (25° C)

Exposure time/h	[MPA] /p.p.m.	E_{corr} /mV	E_{pit} /mV	$\|E_{pit} - E_{corr}\|$ /mV	i_{cp} /A cm^{-2}
0 (ar)	0	−494	122	616	4.7×10^{-6}
	3.5×10^2	−500	153	653	4.1×10^{-6}
	7.0×10^2	−517	208	725	3.4×10^{-6}
	1.0×10^3	−610	370	980	3.2×10^{-6}
	1.5×10^3	−694	np	–	3.0×10^{-6}
	2.0×10^3	−802	np	–	2.9×10^{-6}
	3.0×10^3	−793	np	–	3.0×10^{-6}
59710 (sa)	0	−540	−51	489	6.0×10^{-6}
	3.5×10^2	−560	−20	540	5.6×10^{-6}
	7.0×10^2	−566	70	636	4.9×10^{-6}
	1.0×10^3	−633	150	783	4.4×10^{-6}
	1.5×10^3	−710	450	1160	4.1×10^{-6}
	2.0×10^3	−822	np	–	3.7×10^{-6}
	3.0×10^3	−873	np	–	3.5×10^{-6}
98000 (sa)	0	−603	−115	448	1.2×10^{-5}
	3.5×10^2	−620	−133	487	7.7×10^{-6}
	7.0×10^2	−649	15	664	6.4×10^{-6}
	1.0×10^3	−710	37	787	4.3×10^{-6}
	1.5×10^3	−750	248	1048	4.1×10^{-6}
	2.0×10^3	−840	520	1283	4.1×10^{-6}
	3.0×10^3	−915	np	–	3.5×10^{-6}

ar = as received; sa = service aged; np = no pitting.

characteristics of the as received and service aged specimens. Table 4 shows that with increasing inhibitor concentration E_{pit} for each specimen becomes more positive until a point is reached where no pitting can be induced. The amount of MPA required to inhibit pitting is also seen to increase with the age of the specimen. Additionally i_{cp} for each specimen tends to decrease with increasing MPA concentration.

Amines are known to inhibit pitting in a range of materials [14–16]. Chemisorption onto metal oxide or oxide free surfaces is possible and evidence for this has been obtained in recent work on the adsorption of MPA on low alloy steels in a similar environment [6]. In the present case it is also possible that the inhibitor is adsorbed onto passive and chromium depleted zones surrounding the precipitates and as expected more inhibitor is required to prevent pitting the higher the chromium depletion.

4. Conclusion

Service and artificially aged 347 grade SS S/H tubes behave similarly with respect to general and pitting corrosion although the aging conditions for both types of specimens are different and this may cause a variation in the precipitation process. Pits form in the chromium depleted zones surrounding precipitates. Amine type inhibitors retard pitting and the quantity of inhibitor required to prevent pitting increases in proportion to the age of the specimen.

Acknowledgements

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