Potentiodynamic estimation of the degradation of 347 grade SS superheater tubes Part III: Use of a portable cell for *in situ* evaluation

B. SUN, H. FLITT*, D. P. SCHWEINSBERG[‡]

Corrosion Research Laboratory, Centre for Instrumental & Developmental Chemistry, Queensland University of Technology, GPO Box 2434, Brisbane, Q. 4001, Australia

A nondestructive *in situ* electrochemical polarization method has been evaluated to measure the degradation of 347 grade SS superheater tubes used in fossil fuel-fired power stations. Polarization in 1 M NaOH gave good reproducibility and the measured electrochemical parameter (anodic peak current density i_p) correlated well with increasing [Cr]/[Fe] ratio of sigma/carbide precipitates in both service and artificially aged tubes. The relationship between i_p and the creep damage ratio for artificially aged specimens was established and it is proposed that for plant tests, using the portable cell, tubes should be examined with a view to repair or replacement when i_p exceeds $30\,\mu\mathrm{A\,cm}^{-2}$.

1. Introduction

Austenitic stainless steels (SS) are used extensively as superheater (S/H) tubes in coal-fired power stations. Operating temperatures are approx. 600–650 °C and over time metallographic changes to the alloy occur. For example, for 316 grade SS tubes removed from a Japanese thermal power station, deposition of sigma and carbide phases along grain boundaries was observed [1]. 347 grade SS is used in Australian plants and recent work on aged tubes has shown the presence of similar phases [2, 3]. Such transformations give rise to a deterioration in both mechanical properties (creep resistance, fracture toughness [1]) and corrosion resistance [4, 5].

The inner walls of the S/H tubes are exposed to an aqueous alkaline environment containing a range of impurities [6]. The combination of electrolyte, mechanical stress and changed microstructure can lead to tube failure by intergranular corrosion or stress corrosion cracking [1]. An *in situ*, nondestructive test which can lead to an estimation of the remaining life of a high temperature component is an attractive proposition and a number of electrochemical methods are described in the literature. They involve polarization in an electrolyte using a portable electrochemical cell which is attached to the component during operation or in a shut-down period [7, 8]. Since different test electrolytes may indicate dissimilar metallurgical changes [9] it is desirable that this solution closely resemble the real environment, for example that found inside a SS S/H tube during service.

This paper describes how polarization in 1 M NaOH using the portable cell technique may be applied to the life assessment of aged 347 grade SS S/H tubes. The electrochemical test has been correlated with other measures of material quality deterioration.

2. Experimental details

2.1. Materials

A 347 grade SS S/H tube in the as-received condition had the following composition: Fe 68.62%; Cr 18.31%; Ni 11.56%; Nb 0.70%; S 0.10% and Si 0.70%. Suitable lengths (about 14 cm) of tube were artificially aged in a muffle furnace at 800 °C for set periods (600, 800, 1000, 2000, 3000, 4000, 6000 and 8000 h). Additionally, one piece of tube was annealed at 1050 °C for 2 h and then water quenched to dissolve any sigma phase present. Specimens were then cut from each length of tube for electrodes for laboratory polarization studies [2] and for creep-rupture tests. The remaining sound portion of each piece of tube was used to simulate plant tests with the portable electrochemical cell. Specimens were also cut from failed tubes which had been in service for 59710, 74836, 92823 and 98000 h respectively.

Precipitate phases were identified using 10 M NaOH as etchant and 1 M NaOH was used for polarization studies.

2.2. Apparatus

The electrochemical cell and associated apparatus for laboratory polarization studies have been described previously [2]. The portable electrochemical cell [8]

*Queensland Electricity Commission, 61 Mary Street, Brisbane Q. 4000, Australia.
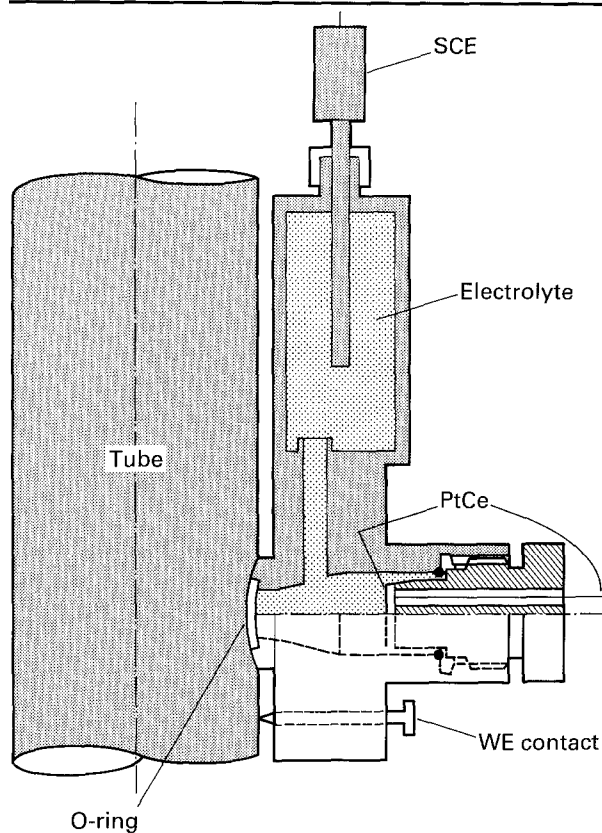[‡]Author to whom correspondence should be addressed.

Fig. 1. Portable electrochemical cell.

was constructed from perspex and is illustrated in Fig. 1. The cell could be clamped on a vertical S/H tube and at the point of contact the cylindrical body of the cell was machined to the curvature radius of the S/H tube. An O-ring provided a leak-free seal and the area of tube exposed to electrolyte (working electrode (WE)) was 0.785 cm^2. The counter electrode was a platinum disc 1.5 cm^2 in area and a small saturated calomel electrode (SCE) was used as reference.

2.3. Procedures

Experimental methods for analysis of precipitates and polarization studies using the laboratory cell (at

$30 \pm 1°C$) are described elsewhere [2]. In experiments with the portable cell the outer surface of the S/H tube was also abraded with different grades of SiC paper and given a final finish with 1200 grade paper. The cell was then clamped on the tube (which was in the vertical position) and filled with 1 M NaOH which had been previously purged with pure nitrogen for 30 min. The WE was immediately polarized in the positive direction at 45 mV min^{-1} to approx. +500 mV vs SCE. Experiments with the portable cell were carried out in air at ambient temperature (23 °C). Creep-rupture tests were done at 650 °C under a load of 148 MPa (Herman Research Laboratory SECV, Victoria).

3. Results and discussion

Previous work [2] using SEM showed the presence of precipitates in specimens cut from service and artificially aged tubes. The precipitates were soluble in alkali and had a double structure consisting of sigma and carbide phases. No such phases were observed in specimens cut from as received and annealed tube. The mean chromium concentration of the precipitates was considerably higher than that for the non-precipitate area in aged specimens or for that in the specimen cut from the as received tube. The increase in the mean [Cr]/[Fe] ratios for precipitates in the various specimens is shown in Table 1. This behaviour was also observed for aged 316 grade SS S/H tubes [1].

The creep damage ratio (ϕ) is expressed as

$$\phi = \frac{t_r - t_a}{t_r} \qquad (1)$$

where t_r and t_a are the times to rupture at a fixed load and temperature for new and aged alloys. ϕ increases with ageing (Table 1) and is a direct measure of alloy quality deterioration. For the artificially aged 347 grade alloy the relationship between the [Cr]/[Fe] ratio and ϕ is shown in Fig. 2 and the former is also

Table 1. Analysis and electrochemical data for service and artificially aged tube specimens

| Specimens	Exposure time/h	[Cr]/[Fe]	$i_p/\mu A\ cm^{-2}$		Creep damage ratio
			Lab. cell	Port. cell	
Service aged (600–650 °C)	59710	0.53	66.3		
	74863	0.59	78.2		
	92823	0.63	85.0		
	98000	0.66	88.2		
Artificially aged (800° C)	600	0.286	32.0	28.6	0.586
	800	0.306	34.4		
	1000	0.326	37.1	29.9	0.782
	2000	0.349	41.7		
	3000	0.386	48.6	35.5	0.802
	4000	0.398	52.4		
	6000	0.437	56.5	40.8	0.814
	8000	0.475	61.7		
Service aged background		0.27	—		
New tube		0.27	27.6		
Annealed tube		—	27.6		
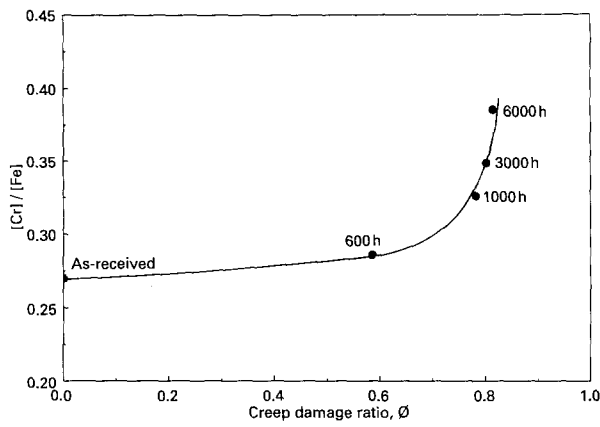
Fig. 2. [Cr]/[Fe] ratio against creep damage ratio for as received and artificially aged 347 grade SS S/H tubes.
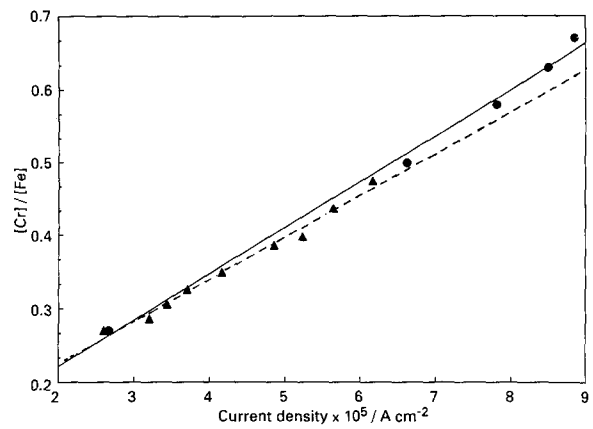

Fig. 4. [Cr]/[Fe] ratio versus peak current density for service aged (●) and artificially aged (▲) specimens.

proposed as a valid measure of SS degradation for aged tubes.

Figure 3 shows typical anodic polarization curves using the laboratory cell for specimens cut from (a) as received or annealed tubes and (b) service or artificially aged tubes. Previous studies [2] indicated that $45\,mV\,min^{-1}$ was an appropriate potential scan rate and that runs should be carried out at a temperature of less than $40\,^\circ C$. A final surface finish using 1200 grade SiC paper was found to give good curve reproducibility for both types of cells. An anodic peak at about $+200\,mV$ vs SCE was obtained for each type of specimen. This peak was also observed for aged 316 grade SS S/H tubes and has been associated with the dissolution of carbides and sigma phases [1–3]. The magnitude of the peak current density i_p was attributed to the amount of sigma and carbide phases formed in precipitates with ageing. The intensity of i_p was essentially the same for the as received and sigma phase-free annealed specimens and this indicates that phases other than sigma are dissolving at this potential. Tests using pure iron and mild steel were free of a

Fig. 3. Typical anodic polarization curves for 347 grade SS S/H tube specimens in 1 M NaOH using laboratory cell: (a) as received, (b) service aged for 74836 h.

peak at $+200\,mV$ vs SCE and this suggests that the observed increase in current density may be associated with oxidation of chromium and/or nickel. The intensity of the peak at approx. $+430\,mV$ vs SCE was also observed to be dependent on exposure time and may be due to oxidation of chromium in the passive oxide film to higher valence compounds [10]. This premise is supported by polarizing in 10 M instead of 1 M NaOH. Only one reaction peak at approx. $+200\,mV$ vs SCE is now observed and this may be due to increased solubility of chromium species in more concentrated alkali solution. Additionally, when an aged specimen is polarized in 1 M NaOH and the scan immediately repeated the peak at $+430\,mV$ vs SCE disappears indicating solution of the chromium oxide film. Figure 4 shows that i_p increases linearly with [Cr]/[Fe] ratio for both service and artificially aged 347 grade SS. The good correlation observed for the two types of aged samples examined (those with long exposure time/low temperature and those with a shorter exposure time/higher temperature) suggests that in both cases the precipitate phases produced are very similar and respond in the same manner when polarized in alkali. The anodic peak current density therefore appears to be a sensitive means of measuring the degradation of this alloy with ageing.
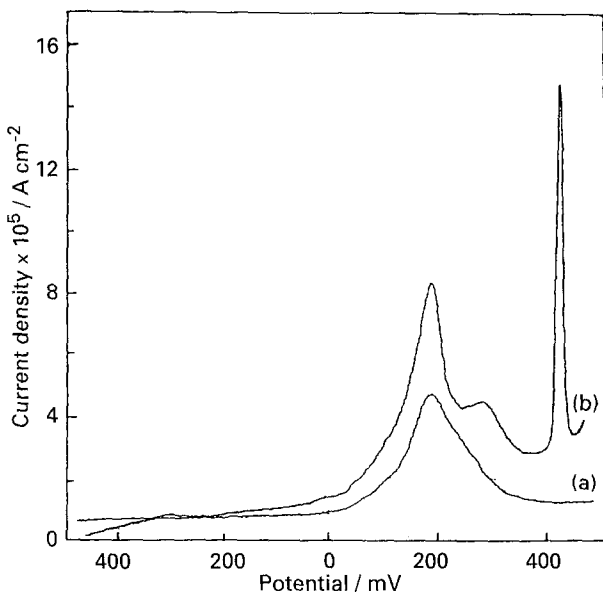
In the present study it was not possible to obtain a large enough sample of each of the service aged tubes in order to prepare specimens for the creep rupture tests. These tests were therefore carried out on specimens cut from tube which had been artificially aged. With respect to Equation 1 it is seen that on ageing t_a will decrease and ϕ approaches unity. It has been suggested for aged 316 grade SS S/H tubes [1] that $\phi = 0.7$ be used as a guide for tube replacement; when this critical value is exceeded a detailed inspection of the tube should be carried out to ascertain whether repair or replacement is warranted. When i_p was plotted against ϕ the critical value of i_p was $35\,\mu A\,cm^{-2}$. The results of plotting i_p against ϕ in this work for the artificially aged specimens using the laboratory and portable cells are shown in Figs 5 and 6, respectively. It is seen
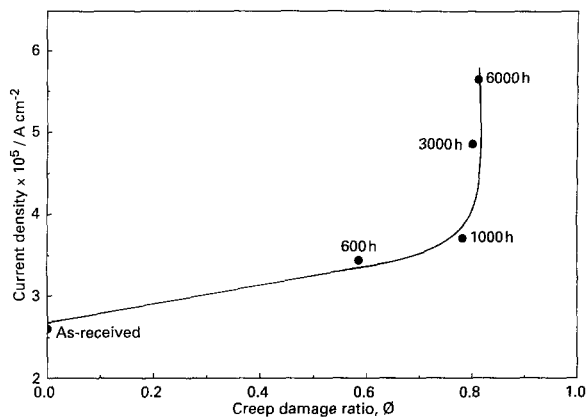
Fig. 5. Peak current density against creep damage ratio for artificially aged specimens using laboratory cell.

Fig. 6. Peak current density versus creep damage ratio for artificially aged specimens using portable cell.

that i_p increases sharply when ϕ exceeds approx. 0.78. The [Cr]/[Fe] ratio also exhibits the same behaviour when ϕ is greater than 0.7 (Fig. 2). A creep damage ratio of 0.7 would therefore appear to be an acceptable, if somewhat conservative critical value to adopt for degradation of this alloy. With the laboratory cell $\phi = 0.7$ corresponds to $i_p = 33\,\mu A\,cm^{-2}$. This value agrees well with that obtained for laboratory studies using 316 grade SS [1]. With the portable cell the magnitude of the recorded current densities was somewhat smaller. This difference is partly due to the lower temperature for the portable cell experiments (23 °C against 30 °C). In this case the critical value of i_p was $30\,\mu A\,cm^{-2}$.

Each of the service aged tubes had experienced creep rupture failure in the plant. Reference to Table 1 shows that in each case using the laboratory cell the critical value of i_p for specimens cut from these tubes had been exceeded.

4. Conclusions

Both artificially aged and service aged 347 grade SS S/H tube undergo similar metallurgical transformations on heating. Creep damage ratio measurements on artificially aged specimens indicate a marked increase in alloy degradation when the ratio exceeds 0.7 and this may be used as a guide for tube repair/replacement. Anodic polarization of tubes using a portable cell is also feasible as a means of measuring deterioration and the corresponding critical value of the measured electrochemical parameter, the anodic peak current density, is $30\,\mu A\,cm^{-2}$.
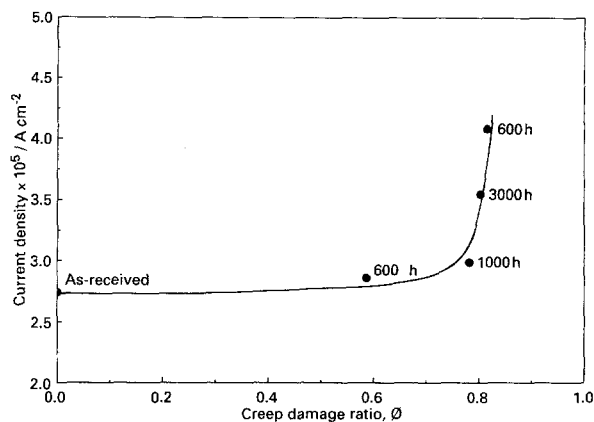
Acknowledgements

References

[1]   Y. Saito, T. Shoji and H. Takahashi, 'Proceedings of an International Conference on Advances in Material Technology for Fossil Power Plants', (edited by R. Viswanathan and R. I. Jaffee), ASM International (1987), p. 367.
[2]   D. P. Schweinsberg, B. Sun, M. Cheng and H. Flitt, *J. Appl. Electrochem.* **23** (1993) 1097.
[3]   D. P. Schweinsberg, B. Sun, M. Cheng and H. Flitt, *Corros. Sci.*, in press.
[4]   D. P. Schweinsberg, B. Sun and V. Otieno-Alego, *J. Appl. Electrochem.*, in press.
[5]   J. H. Potgeiter, *Br. Corr. J.* **27** (1992) 219.
[6]   O. Jonas, *Mat. Per.* **24** (1985) 9.
[7]   T. Shoji and H. Takahashi, in 'Life Extension and Assessment of Fossil Power Plants', (R. Dooley and R. Viswanathan eds.), EPRI CS5208, Electric Power Research Institute, Palo Alto, CA (1987) 745.
[8]   Y. Saito, T. Shoji and Y. Watanabe, *Trans. Japan Soc. Mech. Eng.* **57** (538) (1991) 1442.
[9]   G. S. Vas and V. B. Rajan, *Corrosion* **43** (1987) 576.
[10]   N. Sato and G. Okamoto, 'Comprehensive Treatise on Electrochemistry', (edited by J. O'M. Bockris, B. E. Conway, E. Yeager and R. E. White) **4** (1981) p. 193.