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Potentiodynamic estimation of sensitization of 347 grade SS superheater tubes
Part I: Effect of surface finish, scan rate and solution temperature

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A nondestructive electrochemical method for estimating the degradation of 347 stainless steel superheater tubes has been investigated using basic electrolytes. It was found that Cr/Fe concentration ratio and the anodic peak current density corresponding to dissolution of precipitates (carbides and sigma phases) in 1 M NaOH increased with exposure time at elevated temperatures. The peak current density was observed to increase with electrode surface finish, electrolyte temperature and potential scan rate. A scan rate of 45 mV min^{-1}, temperature below 40° C and surface finish using 1200 grade SiC paper or a mirror finish (3 μm diamond paste) is recommended.

1. Introduction

There is much interest in the development of nondestructive methods for the evaluation of the structural integrity and estimation of remaining life of components used at elevated temperatures, e.g. superheater (S/H) tubes in electricity generating plant. A number of nondestructive methods such as Auger electron spectroscopy [1–3], analytical electron microscopy [4–7], secondary ion mass spectroscopy [8, 9] as well as electric and electromagnetic [10] and chemical and electrochemical techniques [11–15] have been reported.

Electrochemical methods are particularly attractive and have been used for the rapid, quantitative measurement of the degree of material sensitization (DOS), both in the laboratory and in the field [16]. Potentiokinetic reactivation (EPR) techniques in acidic solution, single loop (SL) and double loop (DL) tests, were described by Clarke *et al.* [17] and Akashi *et al.* [18]. More recently an anodic polarization technique in an alkali medium has been developed [19–22].

The method described by Saito *et al.* [21] has been applied to 316 grade stainless steel S/H tubes used in fossil fuel fired boilers. Anodic polarization was carried out in 1 M potassium hydroxide and it was found that the magnitude of the anodic peak current density reflected the degree of grain boundary brittleness resulting from grain-boundary precipitates of carbides and sigma phase [20, 21]. This paper describes results obtained when the method was applied to 347 grade stainless steel S/H used tubes which had failed in service in a SE Queensland coal fired power station and to a specimen cut from a new tube which was artificially aged in a furnace. Initially the effects of potential scanning rate, solution temperature and electrode surface finishing on the anodic current density have been investigated. Scanning electron microscopy (SEM) and energy dispersive analysis (EDA) were also used to estimate the degree of sensitization and the results have been compared with the measured electrochemical parameter.

2. Experimental details

2.1. *Materials*

The new 347 grade stainless steel S/H tubing was supplied by the Queensland Electricity Commission (QEC) and had the following nominal composition: 0.08% C, 17–19% Cr and 9–13% Ni. All reagents were research grade and distilled deionized water was used throughout. 1 M KOH and 1 M NaOH diluted from 10 M stock solution were employed as the electrolyte for the potentiodynamic tests.

The working electrodes (WE) were cut from a new, four used (after 59 710, 74 863, 92 823 and 98 000 h) and an artificially aged S/H tube and mounted in epoxy resin [23]. The artificially aged specimen was prepared by heating the alloy at 800° C for 600 h (Larson–Miller parameter = 24.44) in a furnace. The area of the WE varied between 0.2–0.4 cm^2. The counter electrode was a 10 mm dia. platinum disc also mounted in epoxy resin.

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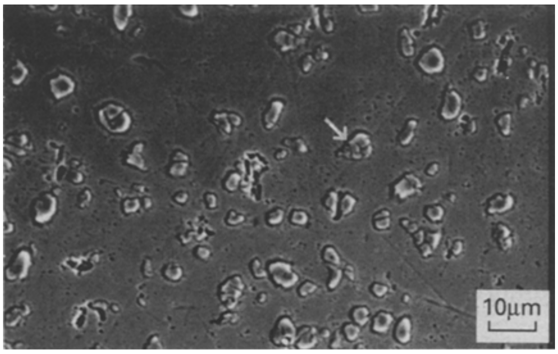

Fig. 1. SEM of a 347 grade stainless steel specimen cut from a used tube (74 863 h).

2.2. *Apparatus*

The anodic polarization studies were carried out using Wenking LB 75L potentiostat interfaced with a personal computer and an AFRDE4 potentiostat (Pine Instrument Company) coupled with an *X–Y* recorder. A potentiometric recorder was used for rest potential measurements. The electrochemical cell consisted of a 500 mL RB flask fitted with a perspex lid which had two 'stirrups' to hold the working and counter electrodes and two openings to accommodate the Luggin capillary for the reference electrode (SCE) and nitrogen gas bubbler. The cell was suspended in a controlled constant temperature water bath.

2.3. *Procedures*

The WE was polished successively with silicon carbide paper (600 to 1200 grade) and then given a mirror finish with diamond paste (3 and 1 μm). It was then degreased in methanol, rinsed in distilled water and quickly placed in the electrolyte which had been purged with purified nitrogen gas for 30 min. In some cases the system was allowed to attain a steady rest potential (approximately 30 min) before polarization. In other cases the WE was immediately polarized in the positive direction using a range of scan rates between 15 and 75 mV min^{-1} at 30° C. The electrolyte temperature was also varied between 20 and 55° C and each of these runs was done at potential scan rate of 30 and 45 mV min^{-1}, respectively.

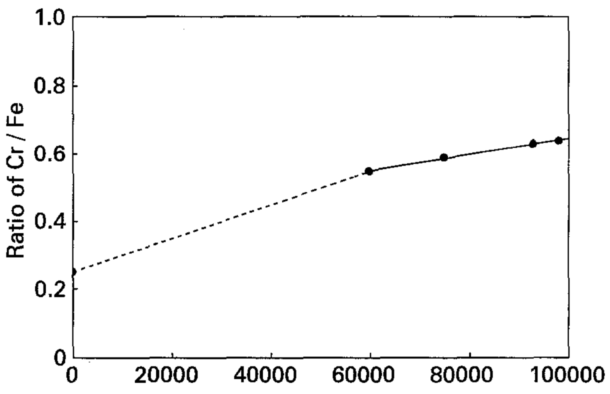

Fig. 2. Cr/Fe concentration ratio vs exposure time for new and used 347 grade stainless steel S/H tubes.

Observation and analysis of precipitates was carried out using SEM and EDA (JEOL JXA-840 A). The specimen was polished as before, connected to the positive terminal of a 3 V dry cell and then etched in 10 M KOH for 0.5 s. At least ten precipitate phase zones were then selected for analysis of chromium and iron contents. Ten different positions in each zone were analysed and the results were averaged. The 'background' concentrations of Cr and Fe were obtained by carrying out analyses on specimens cut from both failed and new tubes.

3. Results and discussion

Figure 1 shows the electron micrograph of a 347 grade stainless steel sample cut from a used tube which had failed after 74863 h in the power station. Etching in 10 M KOH revealed the presence of precipitate phase zones (arrow) in the failed tubes which were similar to those observed by Saito *et al.* [22] for 321 grade S/H tubes. No such zones were visible in the specimen cut from the new tube. Analysis of these zones showed them to be rich in chromium suggesting mixtures of carbides and sigma phases [22]. For example, the Cr/Fe concentration ratio for zones in the above sample had an average value of 0.59 compared with an expected background value of approx. 0.25. Figure 2 shows the results of plotting tube service life versus the mean Cr/Fe concentration ratio for the precipitate zones in the used tubes. The ratio for a new tube (corresponding to zero hours) is also included. At this stage no samples are available for tubes exposed for periods shorter than approx. 60 000 h. A straight line can be drawn through the data for the four used tubes indicating a regular increase in carbide/sigma phase precipitates with service life. The work of Saito *et al.* [22] on SUS 316 grade S/H tubes suggests that there is a critical exposure period required before the Cr/Fe concentration ratio begins to increase above that for a new tube and the same mechanism may be operative here.

Typical results of anodic polarization in 1 M NaOH of specimens cut from a new and failed tube (scan rate

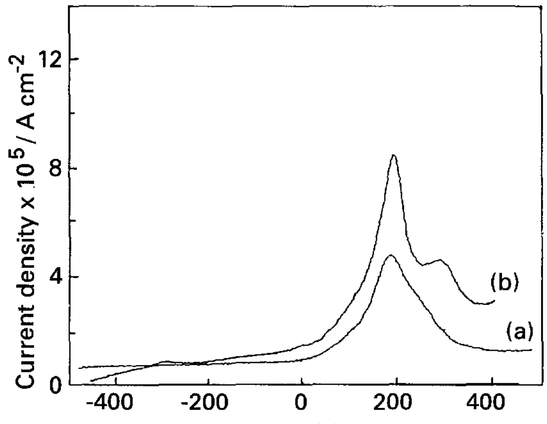

Fig. 3. Polarization curves for 347 grade stainless steel S/H tube specimens in 1 M NaOH solution with a scanning rate of 30 mV min^{-1}: (a) new tube and (b) used tube exposed for 74 863 h.

$30\,\mathrm{mV\,min^{-1}}$) are shown in Fig. 3 (a) and (b). An anodic peak at about +200 mV vs SCE was observed for both the new and used tubes and a further small peak at approx. +290 mV was exhibited for each used tube. Saito *et al.* [22] reported a peak in approximately the same position on anodic polarization in 1 M KOH for specimens cut from new and used 316 grade S/H tubes. The magnitude of the anodic peak current density at +200 mV (i_p) was attributed to the amounts of carbides and sigma phases formed in the alloy. It can be seen in Fig. 3 that i_p for the used 347 grade S/H tubes is much greater than that for a new tube under same test conditions and this indicates an increase in the amount of precipitates with service exposure time for tubes constructed from this alloy. As for the Cr/Fe concentration ratio versus time data a good straight line can be drawn through the corresponding i_p values for each of the used tubes (Fig. 4). Once again a critical exposure period is suggested before i_p increases above its threshold value of approx. $4.7 \times 10^{-5}\,\mathrm{A\,cm^{-2}}$. The results indicate that i_p may be used as a measure of the degree of sensitization of 347 grade stainless steel.

1 M KOH solution was recommended by Saito *et al.* as the electrolyte for the polarization tests but in this study the i_p values were found to be not as reproducible as those obtained when 1 M NaOH was used (RSD approx. 15% against 1.5%). In addition the peak current density obtained in KOH is higher than that in NaOH. These effects are not fully understood and may be due to the influence of bicarbonate ion which is particularly soluble in KOH solution. Addition of a small amount of carbonate ion (5×10^{-3} M to 1 M NaOH) was observed to result in an increase in i_p while a larger addition (5×10^{-2} M) tended to reduce the magnitude of the peak.

3.1. *Effect of scan rate*

The potential scan rate is also an important parameter in the polarization test. The effect of scan rate on i_p for a new, used (92 823 h) and an artificially aged tube at 30° C is shown in Fig. 5. Each point is the mean of at least 3 runs and the RSD was observed to increase with increasing scan rate from about 1.5% up to a maximum of about 3%. The mean peak current density is seen to increase with scan rate for each class of sample and the difference in values between the new and the artificially aged samples is seen to be quite small when the scan rate is less than $30\,\mathrm{mV\,min^{-1}}$. This phenomenon is probably due to there being more time for general dissolution over the entire specimen area at a low scan rate. However, when the scan rate is increased dissolution of precipitate zones is preferred and the rate of increase in i_p is slowed. A scan rate for maximum difference between new and degraded material, e.g. $45\,\mathrm{mV\,min^{-1}}$, should be chosen for the electrochemical tests.

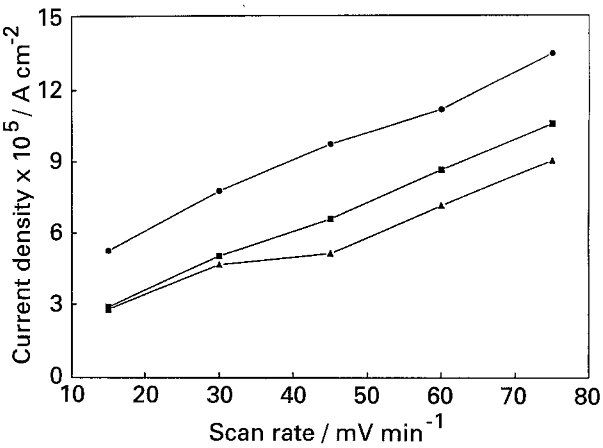

Fig. 5. Effect of scan rate on peak current density for 347 grade stainless steel S/H tube specimens in 1 M NaOH at 30° C. Key: (▲) new; (■) aged; (●) used.

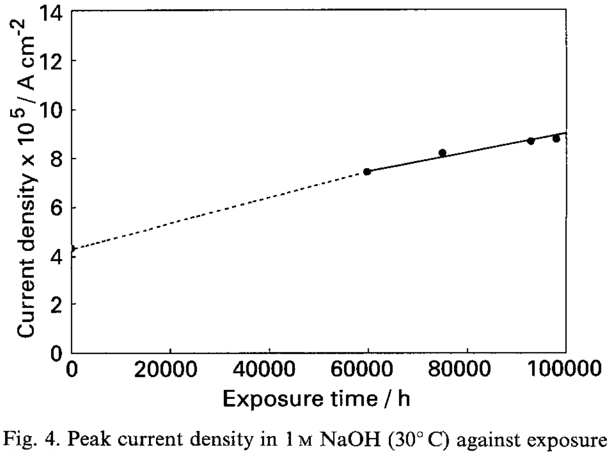

Fig. 4. Peak current density in 1 M NaOH (30° C) against exposure time for 347 grade used stainless S/H steel tube specimens.

3.2. *Effect of temperature*

The effect of electrolyte temperature on i_p was ascertained at 30 and $45\,\mathrm{mV\,min^{-1}}$ and at both scan rates i_p was observed to increase with temperature. This trend is shown in Fig. 6 ($30\,\mathrm{mV\,min^{-1}}$) for a tube exposed for 92 823 h. However, for the artificially aged and new samples, the peak current density value reached a maximum and then decreased slightly at both scan rates. The increase in i_p is similar to that observed in previous reports [17, 24] and is probably due to an increase in the dissolution and diffusion

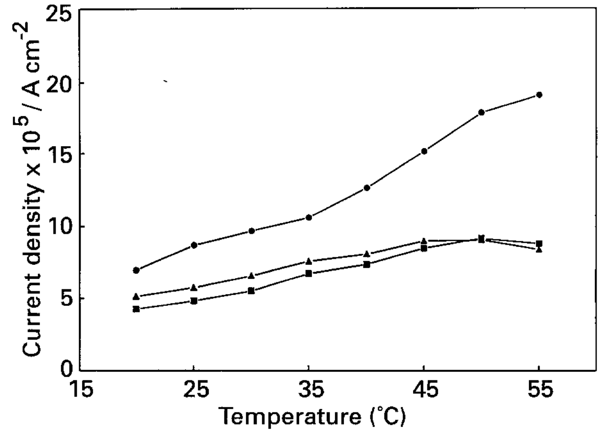

Fig. 6. Effect of electrolyte temperature on peak current density for 347 grade stainless steel S/H tube specimens in 1 M NaOH at a scan rate of $30\,\mathrm{mV\,min^{-1}}$. Key: (▲) new; (■) aged; (●) used.

Table 1. The effect of electrode surface finish on peak current density for failed 347 grade stainless steel tube specimen in 1 M NaOH solution

Surface finish	*Current density/A cm^{-2}*	*Standard deviation* (σ)
600 SiC	9.986×10^{-5}	8.928×10^{-6}
800 SiC	9.632×10^{-5}	6.147×10^{-6}
1200 SiC	9.167×10^{-5}	2.946×10^{-6}
3 μm diamond paste	8.962×10^{-5}	1.499×10^{-6}
1 μm diamond paste	8.830×10^{-5}	1.178×10^{-6}

rates of the carbides and sigma phases at elevated temperature. It was also found, particularly for the new and artificially aged samples, that the reproducibility of i_p decreased markedly at 45° C and a scan rate of 30 mV min^{-1} and at 40° C for a scan rate of 45 mV min^{-1}. It can also be seen from Fig. 6 that due to the flattening of i_p at elevated temperatures, there is an optimum temperature at which the test should be performed (in this case approx. 40° C) especially for new and artificially aged specimens.

3.3. *Effect of surface finish*

The electrode surface finish also affects the magnitude and reproducibility of the peak current density. The results for a used tube (92 823 h) polarized in 1 M NaOH solution are shown in Table 1. It was found that i_p increased with increasing surface roughness and this is probably due to the increase in true surface area with increasing roughness and the presence of a large number of sharp ridges which would be expected to have a high rate of dissolution. A similar phenomenon for the acid corrosion of stainless steel was reported by Majidi *et al.* [24]. The difficulty in reproducing a given area would also increase with the use of a coarser abrasive and this would account for the increase in standard deviation observed with increasing surface roughness. Acceptable reproducibility is achieved using either 1200 grade SiC paper or by reducing to a mirror finish with either 3 or 1 μm diamond paste.

4. Conclusion

This work shows that anodic polarization in 1 M NaOH has promise as a rapid, nondestructive diagnostic method for estimating sensitization of 347 grade stainless steel S/H tubes in power stations. The linear relationship observed between the measured parameter (peak current density) and exposure time for used tubes indicates that i_p may be used to assess the degree of sensitization due to carbide and sigma phase formation. The reproducibility of i_p is affected by surface finish and also possibly by HCO_3^- when KOH is used as electrolyte, accordingly NaOH is recommended. Temperature and potential scan rate are also important parameters and need to be optimized for best results if the technique is to be applied on a routine basis in the plant. The extra effort required to produce a mirror finish on the specimen is considered unnecessary for field application of the technique.

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