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Comparison of stress corrosion cracking susceptibility of thermally-sensitized and proton-irradiated 304 stainless steel using electrochemical noise techniques

L.H. Wang [a,*], J.J. Kai [b], C.H. Tsai [b], C. Fong [a]

[a] Materials Research Laboratories, Industrial Technology Research Institute, Bldg. 52, 195-5 Chung Hsing Rd., Section 4, Chutung, Hsinschu, Taiwan 310, Republic of China

[b] National Tsin-Hua University, Hsinchu, Taiwan, Republic of China

Abstract

The effects of irradiation on the stress corrosion cracking are examined through C-ring stress corrosion tests on thermally-sensitized and sensitized plus irradiated 304 stainless steels using the electrochemical noise technique. All of the C-ring specimens were bolt-loaded to 30 MPa$\sqrt{m}$ and subjected to an environment of high purity, oxygen-saturated water at 288°C. During testing the current signal remained unchanged on the thermally-sensitized 304SS, whereas the current signal of the irradiated specimen steadily increased. The increased current was attributed to the advancement of intergranular stress corrosion cracks which was subsequently verified with scanning electron microscopy. The field emission gun – scanning transmission electron microscopic measurements and radiation-induced segregation model calculations were also carried out in an attempt to correlate grain boundary composition with IASCC resistance. It appears that the pre-existing chromium depletion profiles were not significantly altered by proton irradiation below 0.1 dpa. The increased IASCC susceptibility was probably due to irradiation hardening. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Boiling water reactor (BWR) core internal components have suffered numerous irradiation-assisted stress corrosion cracking (IASCC) problems since the 1970s. Extensive research has been conducted to provide an understanding of this degradation process. Neutron irradiation, reactor water environment, and mechanical loading have been reported as the major factors for IASCC initiation. As neutron dose accumulates, radiation damage is manifested as changes in mechanical properties, phase transformations [1], and radiation-induced segregation (RIS). Although it is generally accepted that RIS plays an important role in IASCC of austenitic stainless steels, the test results are often inconsistent and even contradictory at times [2–4]. Therefore, a systematic study to clarify the effect of RIS on IASCC susceptibility is definitely required, and is the first objective of this paper.

The second objective of this work is the verification of the effect of RIS on IASCC through a series of stress corrosion tests in simulated BWR environments. The stress corrosion cracking characteristics of both irradiated and thermally treated samples were monitored using an electrochemical noise (ECN) technique, which is widely used in monitoring corrosion process, especially in pitting studies [5].

2. Experimental procedure

Tests were performed on sensitized (SEN) Type 304 stainless steel (SS) C-ring specimens (Fig. 1). The Chemical composition of the 304SS is listed in Table 1. All of the specimens were given a sensitizing heat treatment at 650° for 100 h. A notch of 1 mm depth was

* Corresponding author. Fax: +886 35820001; e-mail: liwang@mrl.itri.org.tw.

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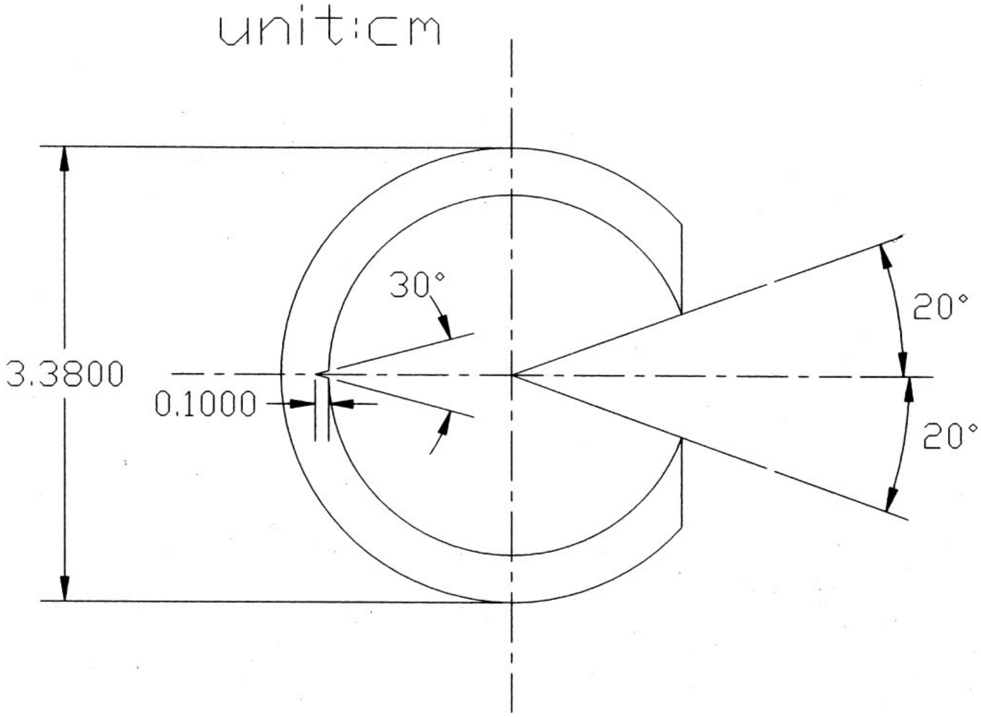

Fig. 1. Dimensions of the C-ring specimen.

Table 1
Chemical composition of the 304 stainless steel

(wt%)	Fe	Cr	Ni	Mn	Mo	P	S	Si	N	C
304	Bal	18.04	8.230	1.490	0.036	0.025	0.002	0.500	0.056	0.047

cut at the central region of the inner radius. The irradiated samples were prepared by bombarding the notched areas with 5 MeV protons at 450°C, using a tandem accelerator, to simulate neutron irradiation damage at commercial BWRs. The irradiated depths were calculated to be 80 μm using TRIM code analysis.

All stress corrosion cracking (SCC) specimens were subjected to an environment of high purity (1 μS/cm), oxygen-saturated water at 288°C. An electrochemical noise (ECN) technique with three electrodes (Fig. 2) was used to monitor the corrosion/cracking behavior. The working electrode, i.e. the test specimen, was bolt-loaded to 30 $\mathrm{MPa}\sqrt{\mathrm{m}}$. The coupling current was measured between the testing specimen and the coupled counter electrode, which was an as-received 304 C ring without loading, via a zero resistance ammeter (ZRA). The electrochemical voltage noise was measured between the testing specimen and a platinum reference electrode, by a high impedance voltmeter. In theory, any electrochemical change occurring on the surface of the test specimen can be detected by the corresponding current and potential variations between the coupled electrodes. Therefore, through examination of the coupled current and potential patterns by various data manipulation methods such as standard deviation, root mean square, resistance noise, etc., the SCC events can be identified.

After preliminary test the loading method was changed to active loading, exerted by the hydraulic pressure within the autoclave by pushing the pull rod outward. A load cell and LVDT were installed on the loading train to measure the applied load and displacement. In addition, a reversing DC potential drop technique was employed to monitor crack advance. However, the reversing DC potential system was shut down periodically in order to avoid interfering with the ECN signal.

3. Results

Fig. 3 shows the coupling current and potential of both the SEN 304 SS and SEN plus 0.01 dpa 304SS specimen. For the irradiated SEN 304 SS, the current

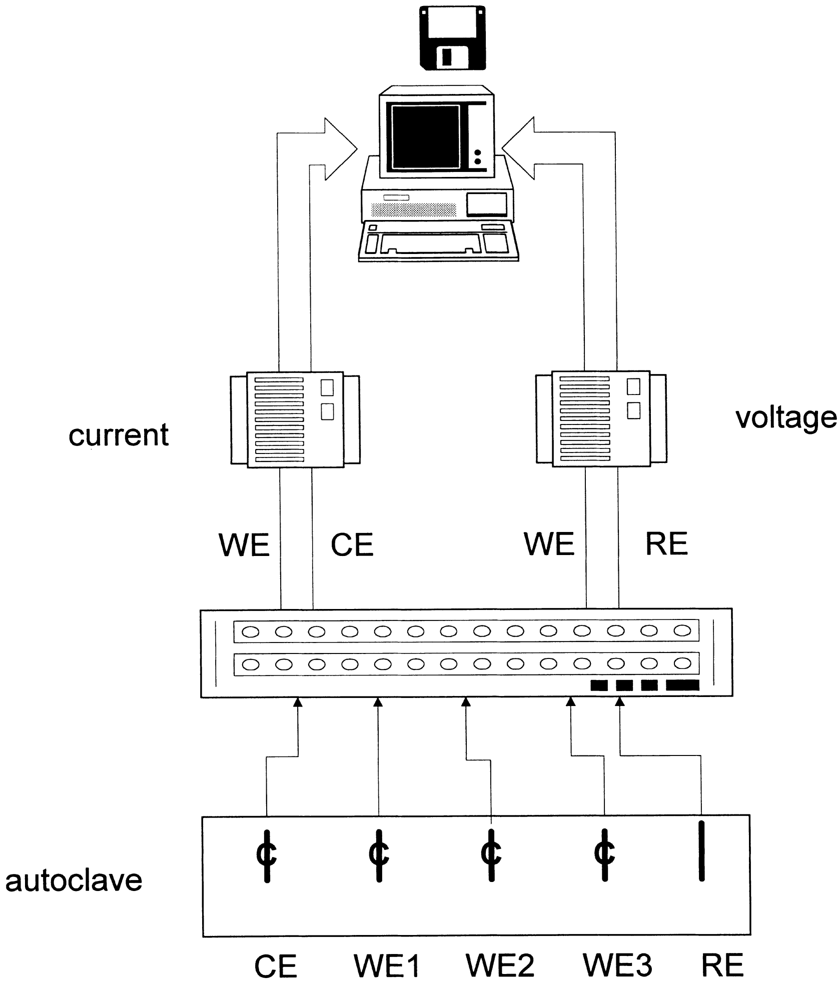

Fig. 2. Configuration of the ECN setup (WE: Working Electrode; CE: Counter Electrode; RE: Reference Electrode).

increased only during the initial test period and subsequently leveled off at a later stage. The rising current might be contributed from two sources: one from the general oxidation current of the working electrode, and another from the dissolution current of the cracked surfaces. However, since the working and counter electrode surface areas were roughly equal, the general oxidation current was cancelled out by the similar level of current contribution from the counter. It is believed the current rise was mainly the dissolution current generated by IASCC at the crack tip. For the SEN 304SS, the level of current increase was significantly lower, suggesting the absence of cracking. The potential of SEN 304 SS and irradiated SEN304 SS both remained relatively unchanged and mainly stayed in the range between −80 and −90 $mV_{(PT)}$. The transient current peaks and corresponding potential drops usually associated with breakage of passive films [6] was not observed in our system.

After test, hairline cracks (Fig. 4(a)) were found on the notch surface of the irradiated sensitized type 304 SS. Typical Intergranular SCC as shown in Fig. 4(b) was observed on the fracture surface by scanning electron microscopy (SEM). As expected from the small level of ECN current increase, no cracking occurred in the SEN 304 SS specimen.

To increase the driving force for crack initiation and propagation, the loading method was changed to active loading. The initial load produced the same K value of 30 $MPa\sqrt{m}$ as was observed with the bolt-loaded batch. The voltage and coupling current variations with the loading conditions of SEN304 + 0.01 dpa are plotted in Fig. 5. As the first load ($K = 30$ $MPa\sqrt{m}$) was applied, the current jumped to a slightly higher value. Then the current steadily went up to about 1 μA within the 25-h testing period. The subsequent three load applications, each about 0.8 mm, are also associated with sudden rises in current value. Compared with the rapid current

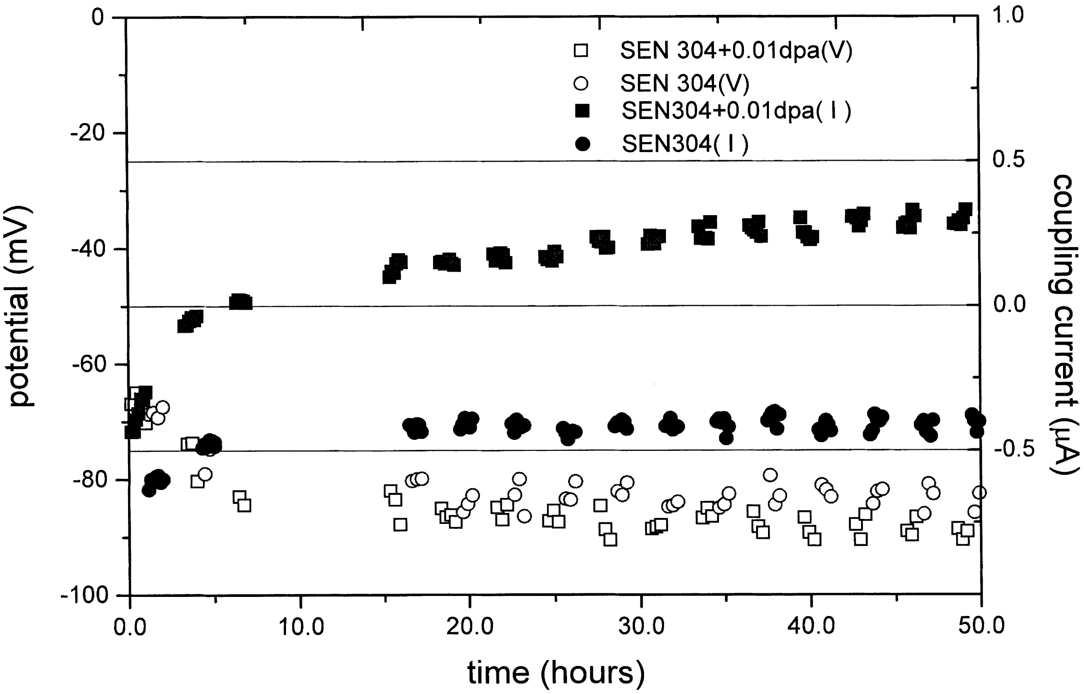

Fig. 3. Coupling currents and potentials of sensitized 304 SS (SEN 304) and irradiated sensitized 304 SS (SEN 304 + 0.01 dpa); V: potential; I: coupling current.

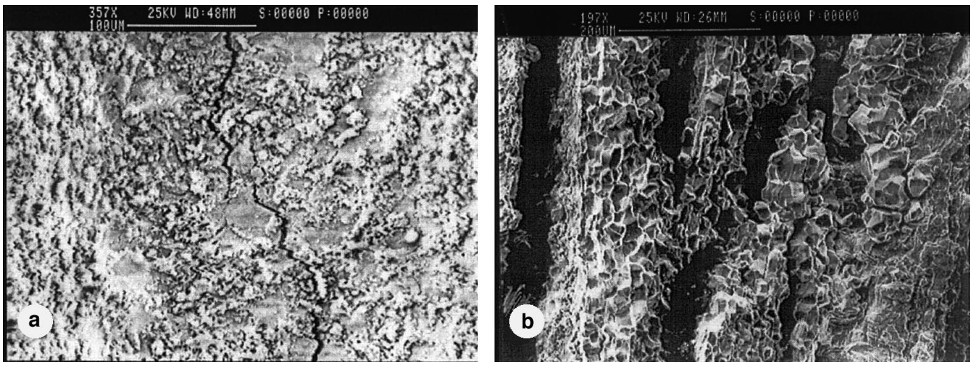

Fig. 4. (a) Hairline cracks found on the notched inner surface of the irradiated sensitized type 304 SS. (b) Typical intergranular stress corrosion cracking on the fracture surface.

increase in the first loading stage, the current increases at subsequent loads were much smaller. The monitoring continued for over 150 h until the current value experienced a sudden drop. After the test it was found that intergranular SCC has completely broken the sample into two pieces. SEM examination confirmed not only the intergranular fracture mode, but also the extensive secondary cracks found in bolt-tightened irradiated SEN304.

To benchmark the ECN signals with the cracking behavior, the thermally sensitized 304 SS also employed another cracking monitoring technique of reversing DC potential drops to measure extent of crack growth. Fig. 6. shows the trends of coupling current, potential, and reversing DC signals within the test period. The current and potential responses first experienced some abrupt transient change in the early startup stage due to initial unstable water chemistry. The first loading ($K = 20$ MPa$\sqrt{\mathrm{m}}$) was applied for about 10 h. Within this period the reversing DC net ratio, potential and current all remained unchanged, suggesting that the crack had not yet been initiated. Once the second loading ($K = 30$ MPa$\sqrt{\mathrm{m}}$) was added to the test specimen, the coupling current and potential immediately

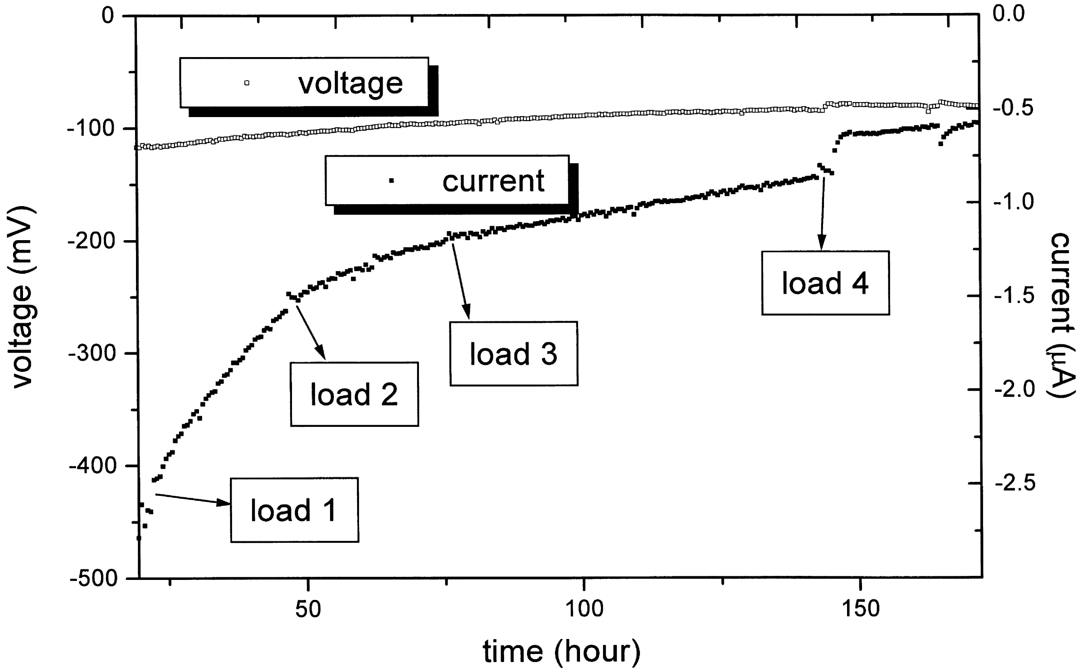

Fig. 5. Voltage and coupling current variations with the loading condition of SEN 304 + 0.01 dpa.

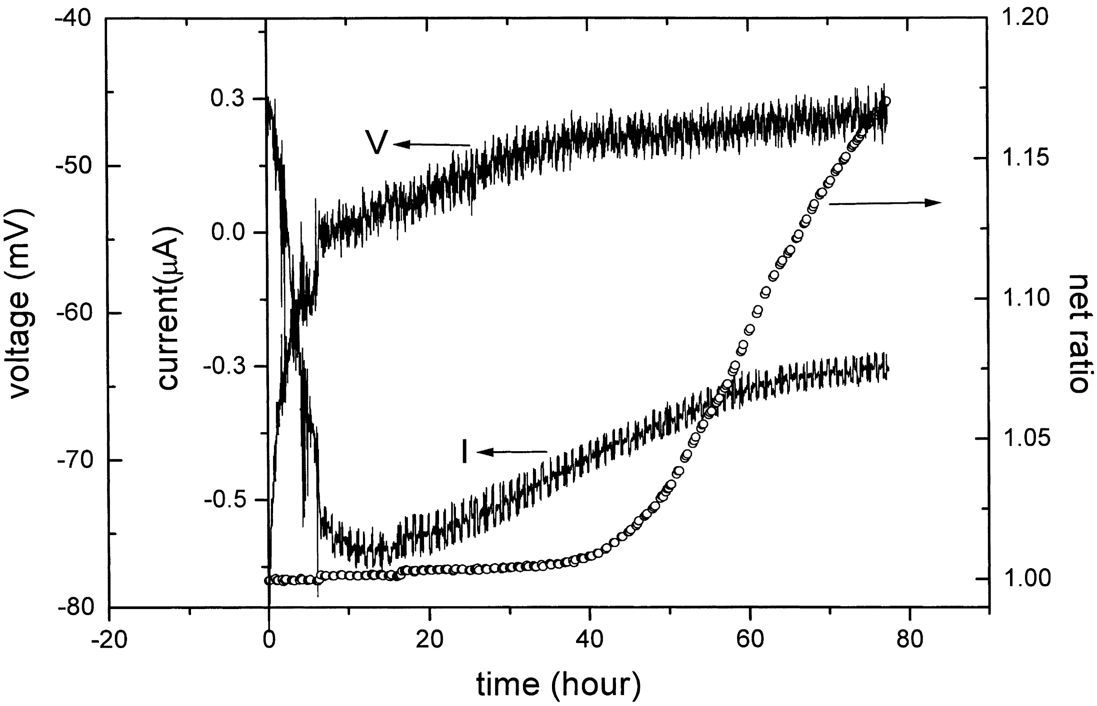

Fig. 6. Trends of coupling current, potential and reversing DC signals of SEN 304 during the testing period.

started to increase with a slower rate than the rate for the irradiated SEN specimen. However, the net ratio stayed stationary for a period of about 15–20 h, and then started to rise. This behavior implies that SEN304 SS required 15–20 h of incubation time to initiate SCC. This is not the case for the irradiated SEN304 SS. The intergranular SCC was verified afterwards by optical microscopic examination. There was no attempt to calibrate the crack length and crack growth rate with reversing DC signals. Summarizing the test results both with passive loading (bolt tightening) and active loading (pull rod driven), it can be concluded that irradiation further enhances the SCC susceptibility of thermally-sensitized alloys.

4. Discussion

It is expected that different dosage of irradiation will cause vastly different RIS profiles with identical preexisting solute concentration profiles, and that this subsequently results in varing degrees of SCC susceptibility. To provide direct evidence for different SCC resistance of SEN 304 SS and irradiated SEN 304 SS, measurement results by the field emission gun–scanning transmission electron microscope are depicted in Fig. 7(a) and (b). Even though the chromium profile of 0.01 dpa-irradiated SEN 304 SS. appears slightly deeper and narrower than the Cr distribution of SEN 304 SS, it is not evident that this would result in significant SCC susceptibility.

The RIS model calculations were further performed to verify the aforementioned results. The basic theory of RIS model based on the inverse Kirkendall effect has

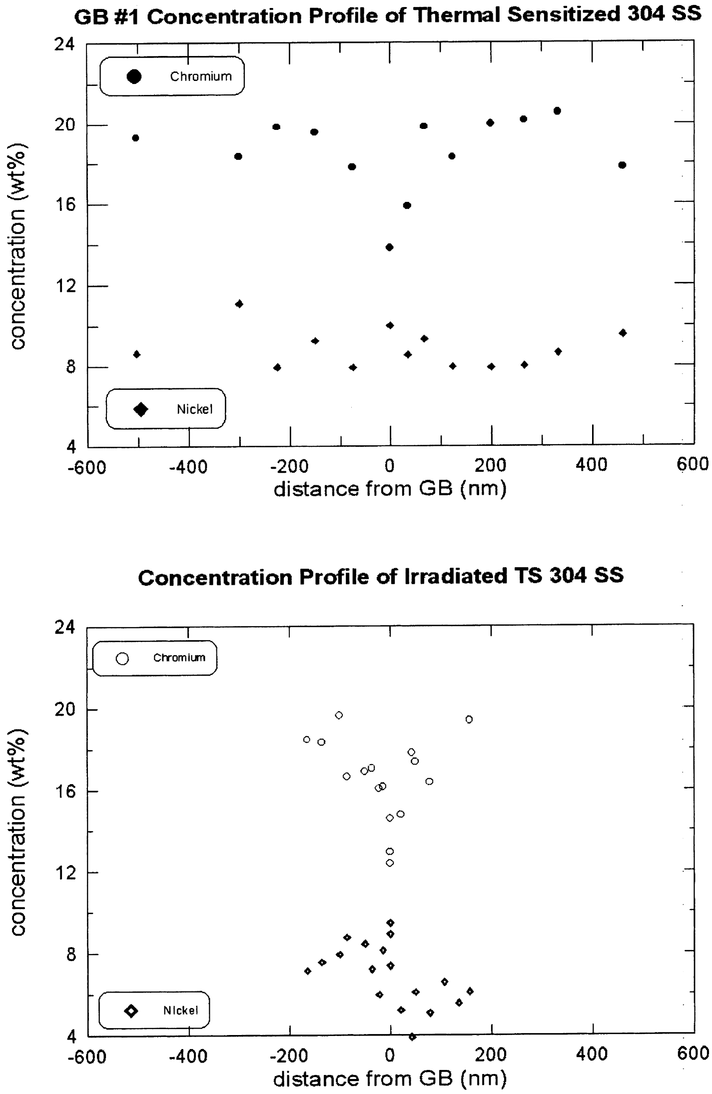

Fig. 7. The chromium/nickel concentration profile of (a) thermally-sensitized (TS) SS and (b) irradiated TS SS as measured by FEG-STEM/EDS, shown as a function of distance from a grain boundary.

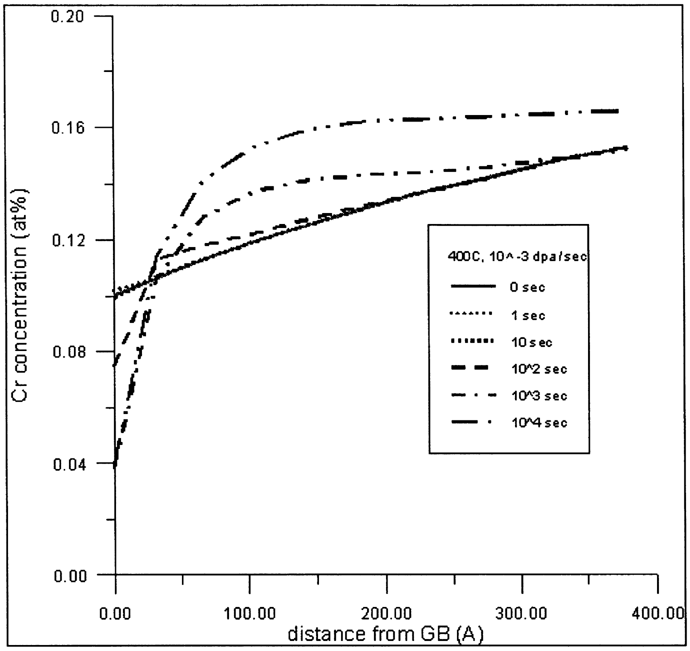

Fig. 8. Results of the RIS model calculation. The wide thermal profile was replaced by the deeper and narrower RIS profile.

been addressed in many papers [7]. The calculated results [8] are shown in Fig. 8. The assumed preexisting thermal Cr depletion profile could only be replaced by the redistribution of RIS above 0.1 dpa (10^2 s.) level. It appeared from the two calculated results that the thermal profile was almost identical to the RIS profile of 0.01 dpa-irradiated (10 s.) specimen. Therefore the cracking susceptibility of IASCC at this level could not be enhanced by the chromium redistribution. The probable cause for the increased IASCC susceptibility at 0.01 dpa irradiation damage was due to the surface hardening effect of irradiation, which substantially shortened the initiation period [9].

The ECN technique at this point could only provide a qualitative tool in differentiating the degree of SCC susceptibility. The reason for the lack of current/potential transient noise may be explained by the assumption that electrons were consumed in adjacent cathodes around the anodic dissolution area. Therefore the current (or electrons) could not be measured at the counter-electrode through the zero resistance ammeter. Mathematical manipulations of the ECN signals through statistical methods also failed to reveal individual cracking events. A possible improvement may be to mask the sample with only the notch region exposed. The challenge is to find masking insulation materials which would be highly adherent and corrosion-resistant in high temperature aqueous environments. Thermally sprayed zirconium oxide may be one of the effective methods. Additional studies are still required for ECN techniques to be used in the quantitative prediction of the SCC trend.

5. Conclusions

1. The irradiated thermally sensitized 304 SS specimens exhibited a greater degree of IASCC susceptibility than did the unirradiated material.
2. ECN results suggest that the coupling current trend can be used a crack propagation indicator. However, the crack initiation point requires further analysis.

Acknowledgements

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