ELECTROCHEMICAL STUDIES ON STRESS CORROSION CRACKING OF INCOLOY-800 IN CAUSTIC SOLUTION
Part I: As received samples

by

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Many non-volatile impurities accidentally introduced into the steam generator tend to concentrate on its surface in restricted flow areas. In this way these impurities can lead to stress corrosion cracking (SCC) on stressed tubes of the steam generator. Such impurities can be strong alkaline or acid solutions. To evaluate the effect of alkaline concentrated environments on SCC of steam generator tubes, the tests were conducted on stressed samples of Incoloy-800 in 10% NaOH solution. To accelerate the SCC process, stressed specimens were anodically polarised in a caustic solution in an electrochemical cell. The method of stressing of Incoloy-800 tubes used in our experiments was the C-ring. Using the cathodic zone of the potentiodynamic curves it was possible to calculate the most important electrochemical parameters: the corrosion current, the corrosion rate, and the polarisation resistance. We found that the value of the corrosion potential to initiate the SCC microcracks was –100 mV. The tested samples were examined using the metallographic method. The main experimental results showed that the increase of the stress state promoted the increase of the SCC susceptibility of Incoloy-800 samples tested under the same conditions, and that the length of the SCC-type microcracks increased with the growth of the stress value.

Key words: alkaline SCC, Incoloy-800, accelerated tests

INTRODUCTION

The steam generator tubes of CANDU power plant have been manufactured of Incoloy-800 – a Fe-Ni-Cr alloy (type UNS N08800). This austenitic alloy has a good general corrosion resistance because it is covered with a passive layer in water at high temperature; however, under certain conditions the stress corrosion cracking (SCC) is observed.

Basically, the SCC appears in the presence of the simultaneous action of a corrosive agent and a mechanical stress.

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The corrosive environment may sometimes appear due to the atypical chemistry of water from the secondary circuit of CANDU nuclear power plant. Another reason for the corrosion occurrence is the concentration of dissolute impurities flowed in within the process of infiltration of the cooling water from condenser.

The stress state can appear in the rolling expansion regions of the steam generator tubes at the joint with the tube plate and in the region of the tube supports. Because of the high speed of heavy water (6-10 m/s) the vibration appears, which is a significant cause of the stress state. The formation of the corrosion products in the limited areas can also generate a significant stress condition. Accordingly, the SCC mechanism can affect both the primary and secondary sides of the steam generator, predominantly the areas containing concentrated impurities.

It is generally believed that the caustic contamination of the steam generator water can appear either from the ingress of river water containing sodium carbonates through leaking condensers or from the release of sodium hydroxide by ion exchange resins [1].

The steam generator damage indicates that the reactor should be shutdown, which brings about the very high costs for its repairing. For this reason, it is necessary to find methods to avoid the SCC appearance in the steam generators tubes.

Under normal conditions, a long time is needed (approximately 10000 hours) before the SCC cracks appear [2]. That is why the accelerated electrochemical corrosion tests must be used to study the susceptibility of Incoloy-800 at SCC.

The C-ring method [3] has been chosen to be the method for stressing Incoloy-800 in the experiments. The ANSYS code was used to evaluate the stress and deformation induced in Incoloy-800 rings [4]. ANSYS is a finite-element analysis package used widely in industry to simulate the response of a physical system to the structural loading as well as thermal and electromagnetic effects. Before the experiments, it was checked by an estimation whether the sample stress condition could be achieved. The tested samples were examined using the metallographic method to prove whether or not there was the appearance of SCC cracks in an alkaline solution.

EXPERIMENTAL

The Incoloy-800 tubes were manufactured with the ASTM SB 407. The external diameter of the steam generator tubes is 15.9 mm and the thickness of the wall is 1.13 mm. The chemical composition of the Incoloy-800, determined by the manufacturer, is given in tab. 1. The mechanical properties of the alloy are shown in tab. 2, according to ASTM SB 407.

Table 1. The chemical composition of Incoloy-800 [wt %]

Fe	Ni	Cr	C	Si	
Balance	30-35	19-23	0.02	0.52	
P	S	Mn	Ti	Cn	Al
0.009	0.004	0.50	0.47	0.01	0.31

Table 2. The mechanical properties of Incoloy-800

Temperature	$\sigma_{0,2\%}$ [MPa]	σ_r [MPa]	E [kN/mm^2]
20 °C	170-205	450-500	198
>300 °C	95	390	180

The C-rings used in our experiments were obtained by cutting the rings of 12 mm in length from the generator tubes. These rings were afterwards compressed by a screw (fig. 1) with the aim to ob-

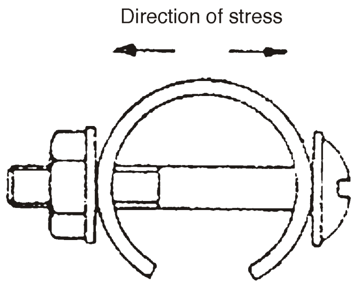


Figure 1. The C-ring to test the susceptibility of Incoloy-800 to SCC (external diameter 15.9 mm, height 12 mm)

tain the yield stress ($\sigma_{0,2\%}$) and ultimate stress (σ_r), of about 413 MPa and 582 MPa, respectively.

The ANSYS code was used to evaluate the stress and deformation induced in Incoloy-800 rings. To check whether the sample stress conditions were achieved, the estimation was made before the experiments. Thus we realized that it was necessary to compress the ring to the diameter of 0.6 mm in order to obtain a value of the yield stress around 413 MPa. To obtain a value of the ultimate stress under 582 MPa, it was necessary to compress the ring to 6.6 mm. The initial and final positions of the rings and screws of both cases are presented in fig. 2.

Figure 3. shows the stress state of both cases. It is known that stress becomes weaker at the ambient temperature. After the tightening of the C-rings, the applied stress stabilised at the value known as the "internal stress". The studies effectuated on Incoloy-800 showed that in practice the stress was stabilised at 80% of the theoretical value [5].

To study electrochemically the susceptibility of Incoloy-800 to SCC we used the potentiodynamic, potentiostatic, and E_{corr}/time techniques. We used the Princeton Applied Research Model 273 Electrochemical System, and several accelerated corrosion tests were carried out. An alkaline solution (10% NaOH) with pH = 13 was introduced into the electrochemical cell containing 3 electrodes (fig. 4, [6]). The electrochemical cell was manufactured of Pyrex glass and had a capacity of one litre. The testing temperatures were the ambient temperature and 85 °C (the maxim temperature supported by electrochemical cell).

When the potentiodynamic method was used, the potential values ranged between –250 mV *vs* E_{corr} and +600 mV *vs* SCE. Because the SCC process needed a long time to be initiated, the scan rate of the potential was 0.2 mV/s. To evaluate the corrosion susceptibility of the system metal/environment to SCC in a specific solution, the most important electrochemical parameters were calculated: the corrosion current (i_{corr}) and the corrosion rate (v_{corr}), using the methods of Tafel slopes and the polarisation resistance.

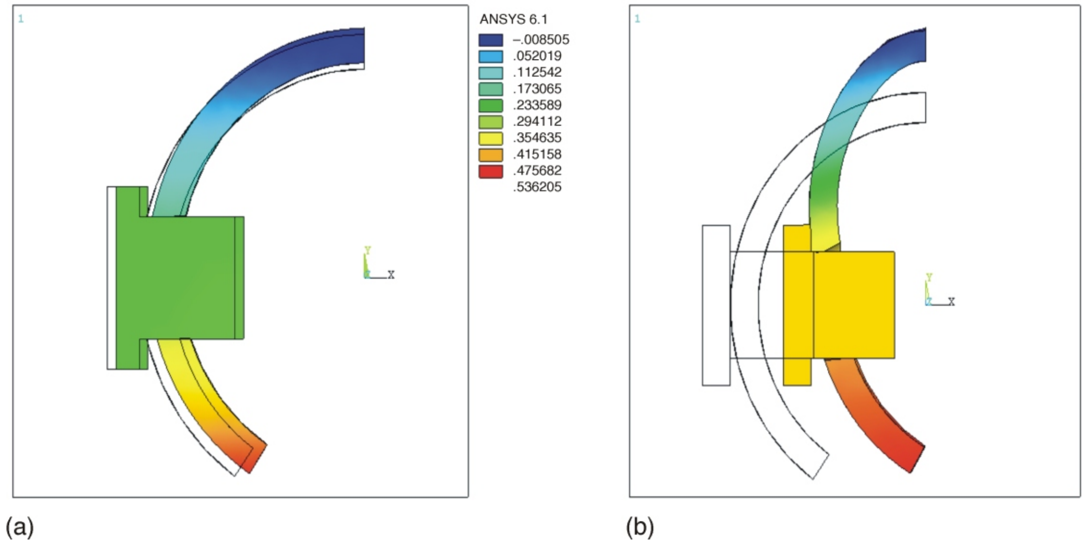


Figure 2. The displacement of the ring in the x direction (a) to obtain a stress around of the yield stress; (b) to obtain a stress under the ultimate stress

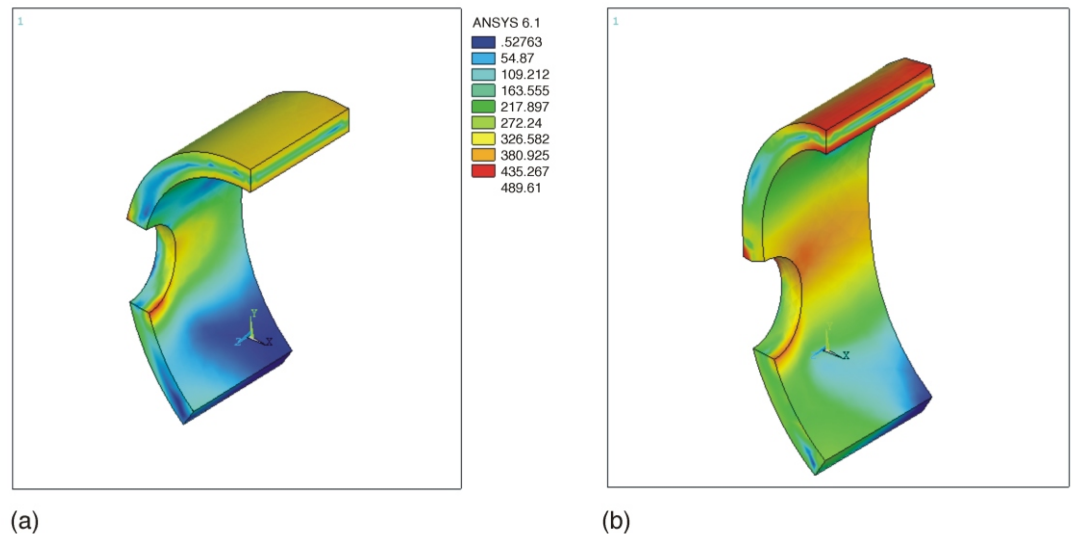


Figure 3. The stress state corresponding to a displacement of the ring with (a) 0.6 mm (around of the yield stress); (b) 6.6 mm (under the ultimate stress)

The selection of potentials for the tests performed at the controlled potentials (potentiostatically) provided a comparison of SCC behaviour in three distinct regions of potentiodynamic (PD) curves: active, active-passive, and passive (fig. 5, [7]). In this way, it was possible to determine the critical potentials characteristic to SCC susceptibility [6]. The potentiostatic method was applied at +80 mV, –100 mV, and –157 mV, the samples being tested for 48 hours at 85 °C in 10% NaOH solution degassed with nitrogen, pH = 13.

Another method consisted in the recording of the variation of the open circuit potential (E_{OCP} or E_{corr}) during the time period. These results are presented as E_{corr}/time curves.

RESULTS

Using the cathodic zone of the potentiodynamic curves we calculated i_{corr}, v_{corr}, and the polarisation resistance R_p. In tab. 3 the experimental values of these electrochemical parameters recorded in 10% NaOH solution on the stressed samples at the maximum value and the unstressed samples at several temperatures are presented.

From the results of tab. 3, we drove following conclusions in the case of samples tested at the same temperature:

– the corrosion potential is less cathodic in the case of unstressed samples; therefore the unstressed

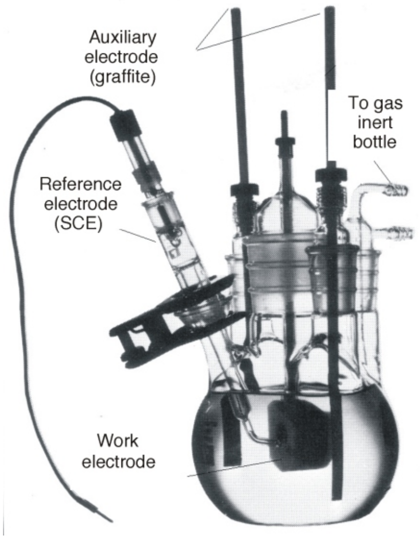


Figure 4. Electrochemical cell [6]

samples are less susceptible at corrosion than the stressed samples, and

– the corrosion rates and the R_p are greater in the case of the stressed samples.

In the case of experiments performed at two temperatures we remarked:

– both the unstressed and stressed samples presented a more negative potential at 85 °C than at 25 °C, and
– the corrosion rates are greater at higher temperature.

The PD curves for one unstressed sample (curve 6) and the respective stressed sample (curve 4) both tested in 10% NaOH at 25 °C are shown in fig. 6. The displacement of anodic current to higher values indicates that the stressed sample is more susceptible to corrosion. The potentiodynamic curves of an unstressed sample (curve 13) and the respective stressed sample (curve 12) tested under the identical conditions, but at 85 °C are shown in fig. 7. In this case, the stressed sample is also more susceptible to corrosion than the unstressed sample. The passivity range of PD curve corresponding to the stressed sample is narrower than that of the unstressed sample. Therefore, the increase of the temperature determined the decreasing of the length of the passivity range of the stressed sample; in other words, the increase of the temperature can increase the alloy susceptibility to SCC.

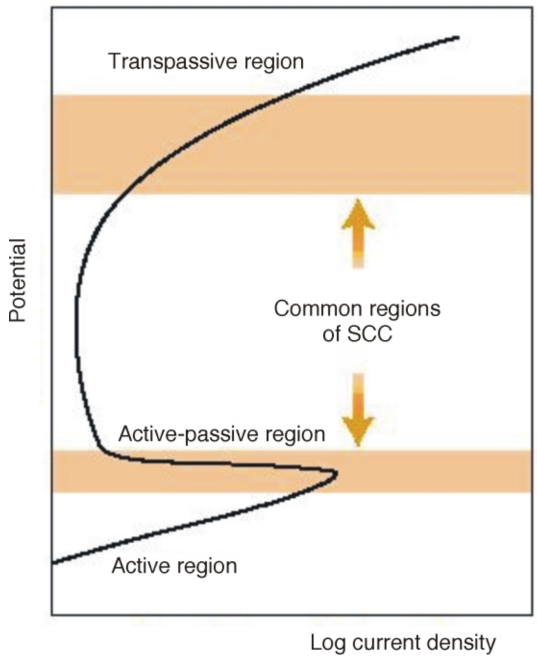


Figure 5. The effect of potential to SCC susceptibility [7]

The E_{corr}-time curves corresponding to the unstressed sample (curve 6) and respectively stressed sample (curve 4) tested for 24 hours at 25 °C in 10% NaOH solution are shown in fig. 8. After about 2 hours the corrosion potential of the unstressed sample decreased down to about −300 mV. Afterwards, the value of the corrosion potential increased slowly maintaining a relatively constant value to the end of the test. The curve 4 corresponding to the maximum stressed sample presents an abrupt decrease of the potential up to −580 mV at the beginning, followed by a few small variations in increase/decrease of the potential. This process is due to the growth of a

Table 3. Experimental values of the electrochemical parameters recorded in 10% NaOH solutions for Incoloy-800 samples

System /curve code	R_p measurements				Tafel slope measurements				
	E [mV]	R_p [kΩ/cm^2]	I_{corr} [μA/cm^2]	V_{corr} [mm/year]	E [mV]	β_c	β_a	I_{corr} [μA/cm^2]	V_{corr} [mm/year]
Unstressed – 25 °C/6	–410	65.7	1.55	0.46	–408	323	604	1.27	0.49
Stressed – 25 °C/4	–424	35.8	1.7	0.6	–422	346	593	1.3	0.55
Unstressed – 85 °C/13	–440	2.5	0.74	0.72	–441	302	164	0.76	0.32
Stressed – 85 °C/12	–554	1.89	1.41	0.54	–537	157	319	1.18	0.49

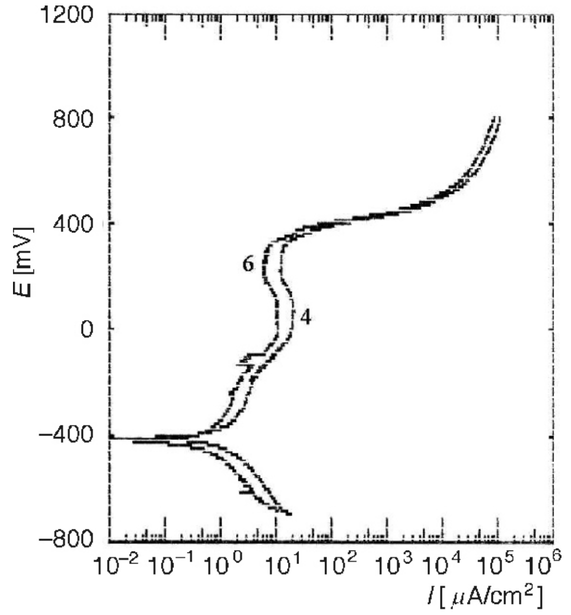


Figure 6. The PD curves for the unstressed sample (curve 6) and stressed sample (curve 4) at room temperature

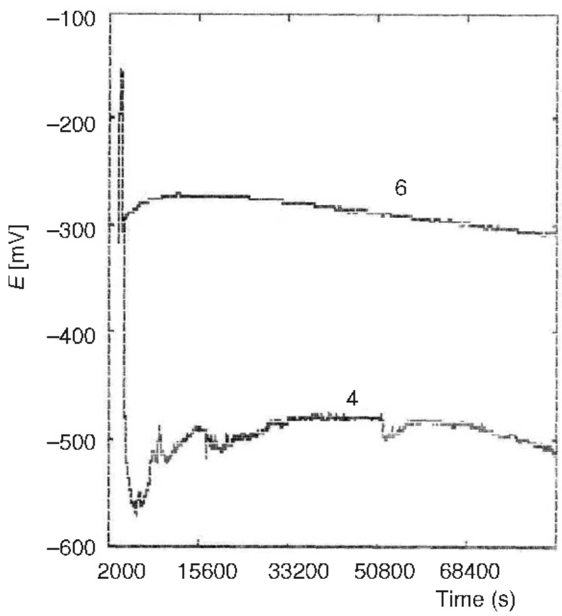


Figure 8. E_{corr}-time curves of the unstressed sample (curve 6) and respective stressed sample (curve 4) tested for 24 hours at 25 °C

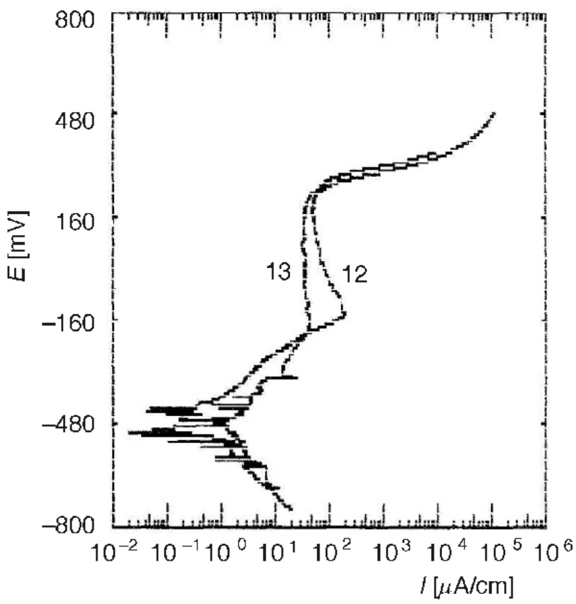
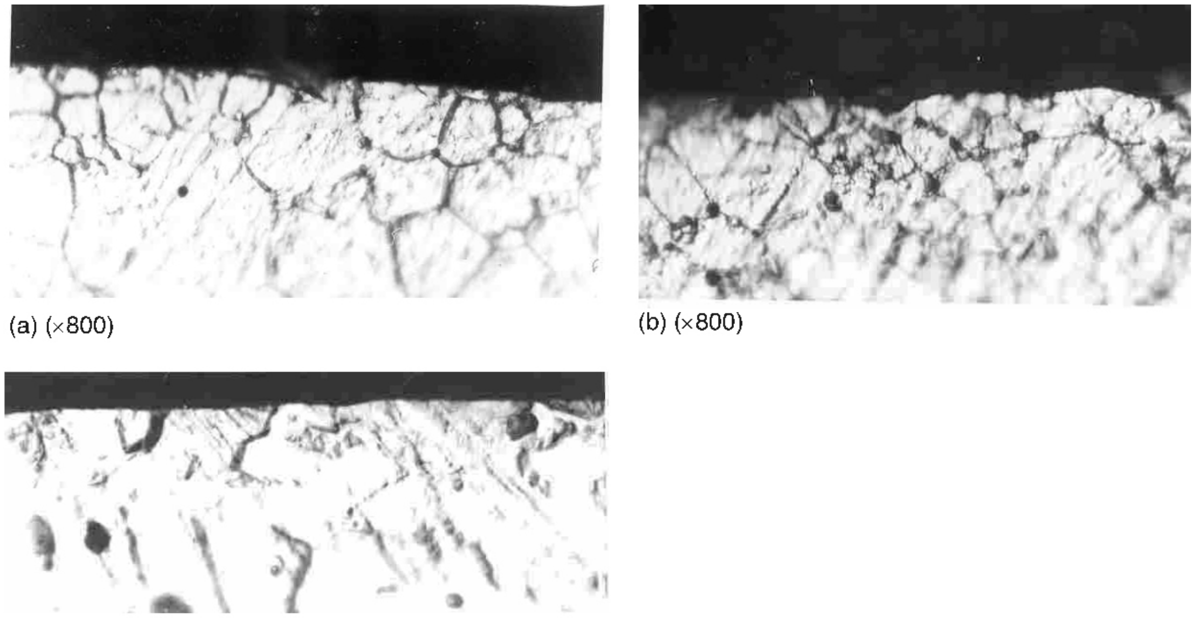


Figure 7. The PD curves for the unstressed sample (curve 13) and stressed sample (curve 12) at 85 °C

layer and its subsequent breaking. The mechanical deformations and the residual stresses influence the deviation of the corrosion potential to more negative values; therefore, the trend to the more negative values of potential is characteristic to an increased susceptibility to SCC of alloys [8].

The stressed samples were tested for 48 hours at 85 °C in a 10% NaOH solution degassed with nitrogen, pH = 13, with different values of the potential: +80 mV, –100 mV, and –157 mV, corresponding to the passive, active-passive, and active region of PD curve 12 (fig. 7). These samples were investigated by the metallographic method. To put in evidence the grain boundaries, the samples were submitted to an electrochemical etching in 10% oxalic acid solution. The samples stressed to the stress maximum value of approximately 490 MPa (under the ultimate stress) and maintained for 48 hours in 10% NaOH solution at 85 °C at –100 mV corresponding to the active-passive region of PD curve showed intergranular microcracks (fig. 9a.). The microcracks spread from the surface into the interior of the sample with an average depth of about 15 m. Another sample tested at the same conditions, but with the potential at –157 mV – the active region of PD curve – showed the incipient microcracks with depths around 10 m (fig. 9b.). The fig. 9c shows the metallographic image obtained at a similar sample tested at +80 mV (the passive region of PD curve). In this case the SCC microcracks did not appear.

To emphasise the influence of stress state on the SCC initiation and the propagation of microcracks, some samples stressed at approximately 390 MPa (around the yield stress) were tested. The test conditions were 10% NaOH degassed solution, temperature of 85 °C, and value of the corrosion potential –100 mV during 10 hours. The appearance of some incipient microcracks with the average depth of about 5 m can be observed (fig. 10).



(a) (×800) (b) (×800)

(c) (×1000)

Figure 9. Microcracks initiated at the surface of the sample stressed at 490 MPa tested 48 hours at 85 °C at following potentials: (a) –100 mV, (b) –157 mV, and (c) +80 mV

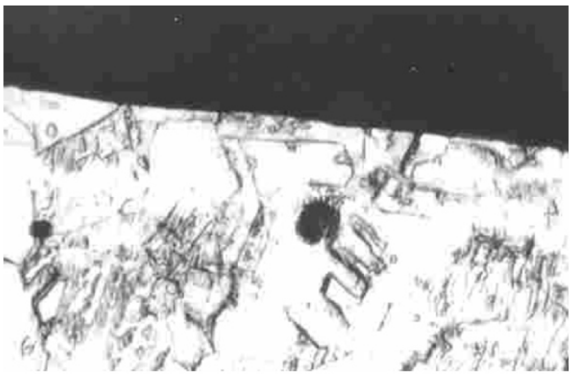


Figure 10. Microcracks at the sample stressed at 390 MPa, tested 10 hours at 85 °C at –100 mV (×1000)

CONCLUSIONS

The stressed samples of Incoloy-800 show a higher susceptibility to SCC than the unstressed samples. At room temperature and at 85 °C the passive range is shorter in the case of the stressed samples than in the case of the unstressed ones.

The increase of the temperature leads to the increasing of the SCC susceptibility of the stressed samples. At 85 °C the passivity tendency is smaller than at the room temperature.

The value of the corrosion potential needed to initiate and propagate the SCC microcracks at the surface of the samples stressed at 490 MPa (tested for 48 hours in a 10% NaOH solution) was –100 mV.

An increase of the stress state promotes an increase of the SCC susceptibility of Incoloy-800 samples tested at the identical temperature and environment conditions. The samples stressed at approximately 390 MPa show some incipient microcracks with depth of about 5 m. On the other side, many incipient microcracks with spreading from the surface deep approximately 15 m may be observed at the samples stressed at 490 MPa.

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ЕЛЕКТРОХЕМИЈСКО ПРОУЧАВАЊЕ ПУЦАЊА ЛЕГУРЕ INCOLOY-800 УСЛЕД НАПОНСКЕ КОРОЗИЈЕ У РАСТВОРУ НАТРИЈУМХИДРОКСИДА ДЕО ПРВИ: УЗОРЦИ У СТАЊУ ИСПОРУКЕ

Многе неиспарљиве нечистоће случајно унете у парогенератор склоне су нагомилавању на његовој површини у ограниченим зонама протока. Ове нечистоће, које су кисели или базни раствори, могу у парогенератору довести до пуцања цеви под притиском услед појаве напонске корозије. Ради оцене утицаја базне средине на напонску корозију парогенератора, обављена су испитивања на претходно деформисаним узорцима легуре Incoloy-800 у 10% раствору натријумхидроксида. Ради убрзања процеса пуцања, деформисани узорци били су у електрохемијској ћелији подвргнути анодној поларизацији у раствору натријумхидроксида. За постизање деформисаног стања цеви у експерименту коришћена је метода С-обруча. Применом катодних зона потенциодинамичких кривих, било је могуће израчунати најзначајније електрохемијске параметре: струју корозије, брзину корозије и отпорност тела поларизацији. Утврђено је да је –100 mV вредност потенцијала корозије за почетак стварања микропрскотина. Тестирани узорци били су испитани металографски. Најважнији експериментални резултати указују да при истим условима испитивања, осетљивост Incoloy-800 на пуцање при напонској корозији расте са порастом степена деформације, као и да се дужина микропрскотине повећава са порастом деформације.

Кључне речи: напонска корозија у базним растворима, Incoloy-800, убрзано испитивање