# Chloride Stress Corrosion Cracking of Incoloy - 800

**ALICE DINU*, VASILE RADU**
Institute for Nuclear Research, 1 Campului Str., 115400 Mioveni, Romania

*To evaluate the susceptibility at chloride stress corrosion cracking of Incoloy-800 used to manufacture the steam generator tubes for CANDU nuclear power plant few electrochemical corrosion tests were conducted in NaCl solution (0.033g/L and 0.33g/L NaCl). The solution concentration ranges were selected starting from the maximum $Cl^-$ concentration accepted in the cooling water in the case of CANDU reactors and allowing the concentrated factors that may appear in areas with restricted flow, by boiling. The C-ring method was used to stress the samples. In order to create the spots of mechanical stress, the mechanical pre-cracks with a depth of 100μm or 250μm were inserted in the samples. The increase of the concentration of chlorine together with the local deformation will lead to a higher susceptibility to stress corrosion cracking. In the solution of 0.33g/L NaCl the cracks are always associated with pits. On the other hand, for the samples tested in 0.033g/L NaCl solution it was often observed that cracks did not start from a pit. In both situations, the cracks propagation is transgranular, while the initiation mode differs: when the crack starts from a pit the initiation is transgranular; in the absence of a pit, the initiation of cracks is intergranular. The threshold value of stress intensity factor that has been evaluated in the paper is $K_{Imax}$=4.58 $MPa{\cdot}m^{-1/2}$.*

*Keywords: Stress corrosion cracking; Incoloy-800 alloy; CANDU steam generator*

Among the corrosion types which can affect the secondary side of the steam generators in nuclear power plants, the Stress Corrosion Cracking (SCC) phenomenon is an insidious form of corrosion because it conducts to a radical change of the mechanical properties, without a significant loss of metal. Therefore, the SCC mechanism can led to a catastrophic failure of components and structures. The wall of Incoloy 800 tubes represents the boundary between the circuit of heavy water (contaminated with radioactive corrosion products) and light water circuit which is non-radioactive. Therefore any crack of tubes involves contamination of the secondary side. This fact has economical consequences as the nuclear power plant stops operations while the tubes are obturated or removed.

Steam generators tubes for CANDU reactors are manufactured from the Incoloy 800 alloy, which has a very good corrosion resistance, due to a protective layer formed on the material surface during the work in water at high temperatures. However, this alloy becomes predisposed to SCC phenomenon in certain environments, which are normally non corrosive, because of the presence of applied stresses.

For a long time, it was supposed that the SCC mechanism appears in areas with restrictive flow only, because of a strong caustic environment. The investigations of the failed tubes that were taken out of service emphasized that this environment is more complex, containing impurities such as $Cl^-$, Pb or silicon aluminates [1]. In the case of CANDU NPPs cooled with river water, an accidental formation of a concentrated corrosive medium becomes possible in the zones with restricted circulation as result of leakages of cooling water from the condenser. Through the boiling process, small quantities of impurities can be concentrated inside of crevice up to $10^3$-$10^5$ times [2, 3]. The presence of a concentred chlorinated environment into crevices leads to a decrease in the pH level and the results is the initiation of intergranular stress corrosion cracking of Incoloy 800 steam generator tubes.

Compared with chemical factors that act in this case, the applied stress has more a contributively role, but not determining role [4]. 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. Cold work, welding and heat-treatment may lead to the important residual stress. In case of steam generator tubes, strong residual stresses appear in the U-bend zone, especially for tubes with a small curvature radius. Also, the existence of corrosion products in the limited area can generate significant residual stresses. Other sources of residual stresses are the thermal gradients between the steam and waterish zone that boot the alternate thermal cycles between dry and wet zones [5]. Separately, these contributions can be not significant. With their effects combined, these contributions can overcame the critical threshold of local stresses to initiate SCC mechanism.

The purpose of this study is to investigate the SCC behaviour of Incoloy 800 alloy in the aqueous environment with *p*H near neutral, contaminated with $Cl^-$. For this purpose we carried out several accelerated corrosion tests using the Princeton Applied Research Model 273 Electrochemical System. Observations of the samples after SCC test using metallographic and scanning electron microscopy were performed. Also, seeing that SCC cracks start form one pit in chlorinated testing environment, the stress intensity factor, along of one pit border, was calculated using FEA-Crack software.

## Experimental part

*Samples preparation*

The sample specimens were prepared in accordance with ISO 7539-5/1996, from Incoloy-800 pipe manufactured conformable ASTM SB 407. The outer diameter of Incoloy 800 tubes is 15.9mm and the wall thickness is 1.13mm. Table 1 shows the chemical composition of Incoloy 800 used in the experimental tests.

It was chosen the C-ring method to apply the stress to the samples [6]. With the aim to obtain the C-rings, rings

* email: alice.dinu@nuclear.ro; Tel.: 0248314000 / 443

**Table 1**
CHEMICAL COMPOSITION OF INCOLOY 800 IN ACCORDANCE WITH THE ACCEPTANCE CERTIFICATE OF PRODUCER (wt%)

| Element | Fe | Ni | Cr | C | Si | S | Mn | Ti | Cu | Al |
|---|---|---|---|---|---|---|---|---|---|---|
| Concentration (wt%) | 42.7 | 33.4 | 21.9 | 0.02 | 0.49 | 0.001 | 0.64 | 0.41 | 0.01 | 0.24 |

**Table 2**
CHARACTERISTICS OF THE TESTING SOLUTIONS

| Solution concentration (NaCl g/L) | Concentrating factor | pH |
|---|---|---|
| 0.033 | $10^4$ | 5.71 |
| 0.33 | $10^5$ | 5.55 |

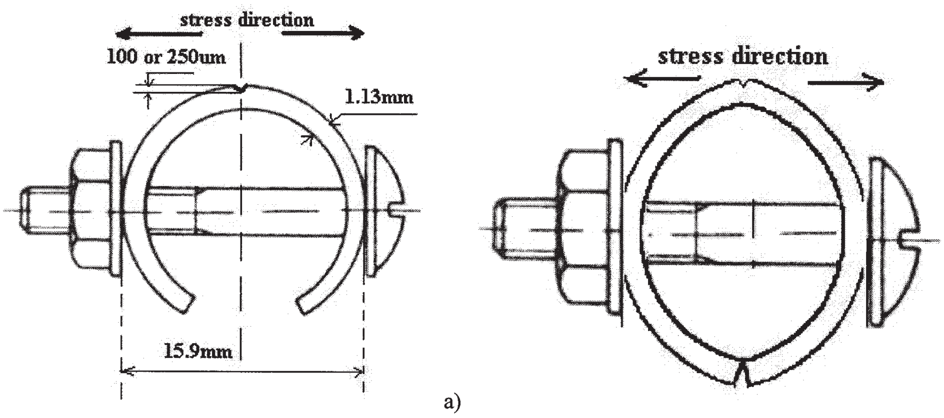



Fig.1. C-ring used to test the susceptibility of Incoloy-800 to SCC: a) unstressed sample; b) stressed sample

with a 12mm height were cut from Incoloy-800 tubes, and then, each ring was split out on generatrix. To obtain some concentrated stress in a certain zone [7], some samples were mechanically pre-cracked. The mechanical cracks had the following depths: one of 100μm and another one of 250μm (fig.1a). The C-ring samples were then compressed using a screw (fig.1b).

The estimation made at room temperature using the ANSYS code revealed that the maximum value of the total deformation was 4.5% in case of samples without pre-crack. The value of the total deformation strongly increases with the depth of mechanical pre-crack: 5% in the case of 100μm and respectively 9.4% in the case of 250μm depth [8]. In both cases, the maximum value of the total deformation was located laterally from the highest point of the mechanical pre-crack.

*Testing environment*

The composition of testing solutions was established starting from the maximum value of chloride ions concentration accepted in cooling water in case of CANDU reactors (1ppb [9]) and taking into account the concentrating factor ($10^3$-$10^5$ [2, 3]) resulted by boiling. Finally, the used concentrations were 0.033g/L NaCl solution and 0.33g/L NaCl solution, having *p*H near neutral (table 2).

*Accelerated tests*

Under normal working conditions, the SCC mechanism requires a long time to initiate. Therefore for the laboratory study of the SCC behaviour of materials it is necessary to use special tests which give the possibility to accelerate the SCC mechanism. The majority of the accelerated tests are based on the electrochemical methods. The test conditions must be carefully chosen in order to influence not the attack mechanism. This must be the same as in the real situation (existing inside of NPP during normal operation) and simulated situation in laboratory.

The accelerated electrochemical corrosion tests were performed using the Princeton Applied Research Model 273 Electrochemical System. The tests were carried out at the ambient temperature and 85°C (the maximum temperature at which the electrochemical cell can operate). The potentiodynamic method as well as the potentiostatic method have been used. When the potentiodynamic (PD) method was used, the potential values ranged between (–600)mVvsEcor, and (+1600)mVvs.SCE (Saturated Calomel Electrode) with a scan rate of the potential of 0.2mV/s. The potentiostatic polarisation tests were carried out only in 0.33g/L NaCl solution for 24 h at an applied potential of +500mVvsSCE. This value of applied potential was chosen in trans-passive region of cyclic polarization curves.

## Results and discussions

*Electrochemical tests*

To evaluate the corrosion susceptibility of the metal/ environment system at SCC in a specific solution, the most important electrochemical parameters were calculated, i.e. the corrosion current ($i_{corr}$), corrosion rate ($v_{corr}$) and corrosion potential ($E_{corr}$). Table 3 shows the values obtained for these parameters which depend on the concentration of the testing solution and on the state of samples. One may observe that the corrosion rate and the corrosion current increase along with the increase in the local deformation, while the corrosion potential shifts towards the electronegative range. The PD curves are presented in. figure 2. The increase in the NaCl concentration leads to an increase in the localised corrosion susceptibility (table 3).

The electrochemical tests at imposed potential of +500mV, performed in 0.33g/L NaCl at 85°C for 24 h, show that the corrosion current is increased as the value of local deformation increases. This behaviour confirms that the SCC susceptibility of Incoloy 800 increases with the augmentation of local deformation (fig.3). The increase and decrease in corrosion current indicates the breaking and reconstruction of the thin oxide layer on the surface of samples. This means that the corrosion agents may get access to the metallic substrate, and the SCC cracks can be initiated. Only in the case of the stressed sample with 250μm depth of the mechanical pre-crack (deformation 9.4%) there are few picks of corrosion current which could indicate the propagation of SCC cracks.

| Solution concentration (NaCl g/L) | Sample characteristics | $E_{cor}$ (mV) | $I_{cor}$ ($\mu A/cm^2$) | $V_{cor}$ (mm/y) |
|---|---|---|---|---|
| 0.033 | without mechanical pre-crack; local deformation 4.5% | -140 | 0.57 | $6\cdot10^{-3}$ |
| 0.033 | mechanical pre-crack 100μm; local deformation 5% | -203 | 12.5 | $130\cdot10^{-3}$ |
| 0.033 | mechanical pre-crack 250μm; local deformation 9.4% | -232 | 15 | $170\cdot10^{-3}$ |
| 0.33 | without mechanical pre-crack; local deformation 4.5% | -176 | 2 | $20\cdot10^{-3}$ |
| 0.33 | mechanical pre-crack 100μm; local deformation 5% | -200 | 7.5 | $80\cdot10^{-3}$ |
| 0.33 | mechanical pre-crack 250μm; local deformation 9.4% | -278 | 18 | $200\cdot10^{-3}$ |

**Table 3**
EXPERIMENTAL VALUES OF THE ELECTROCHEMICAL PARAMETERS RECORDED NaCL SOLUTIONS FOR INCOLOY-800 SAMPLES

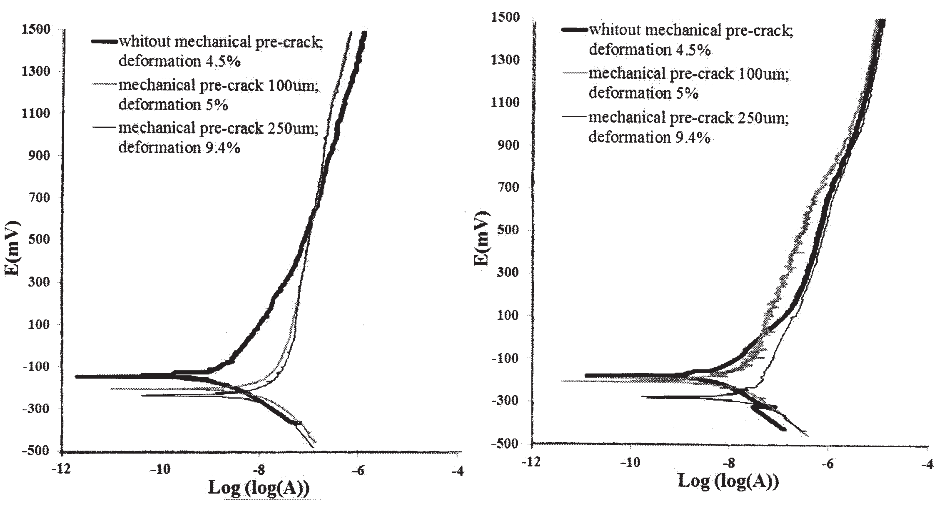



Fig.2. Potentiodynamic curves corresponding to the samples tested at 85$^0$C in NaCl solution: a) 0.33g/L NaCl; b) 0.033g/L NaCl

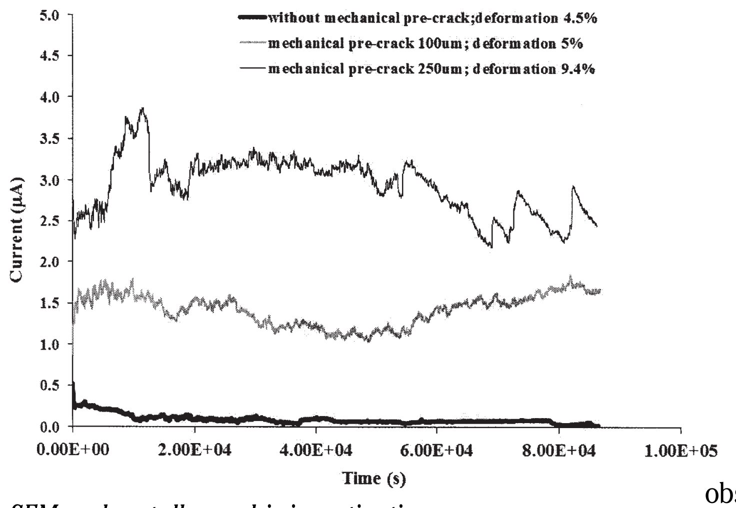



Fig.3. Evolution in time of current in potentiostatic conditions corresponding to the samples with different degrees of local deformation, tested in 0.33g/L NaCl solution, at 85$^0$C and +500mV imposed potential

*SEM and metallographic investigation*

The metallographic investigation emphasized the presence of incipient SCC cracks on the external surface of the samples without a mechanical pre-crack that were tested through the potentiodynamic method (fig.4). Frequently, these SCC cracks start from pits. One may observe how a surface reaction leads to the pit formation, followed by the SCC initiation. Also, there are SCC cracks which are not associated with pits. Certainly, in the absence of pits, the SCC cracks are initiated from the precipitates or from the inclusions present at grains boundary.

In all cases, the SCC cracks are oriented perpendicularly on the direction of applied stress. The increase in the $Cl^-$

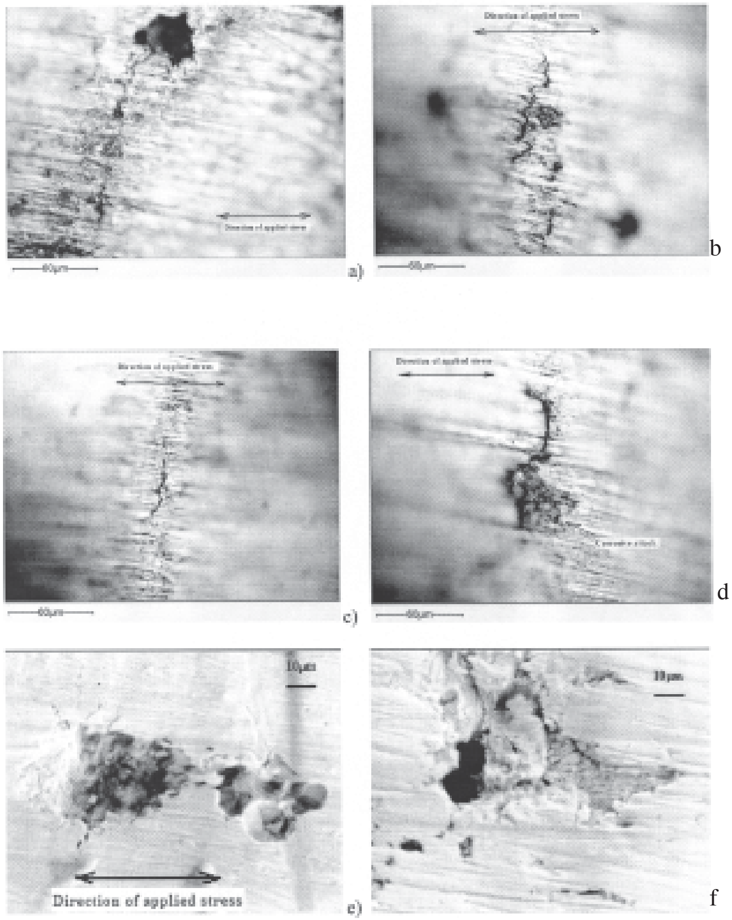



Fig.4. SCC cracks initiated on external surface of Incoloy 800 samples without mechanical pre-crack (deformation 4.5%), and tested by PD method in 0.33g/L NaCl solution (a, c – metallographic images; e- SEM image (x600), and 0.033g/L NaCl solution (b, d – metallographic images; f- SEM image (x600)

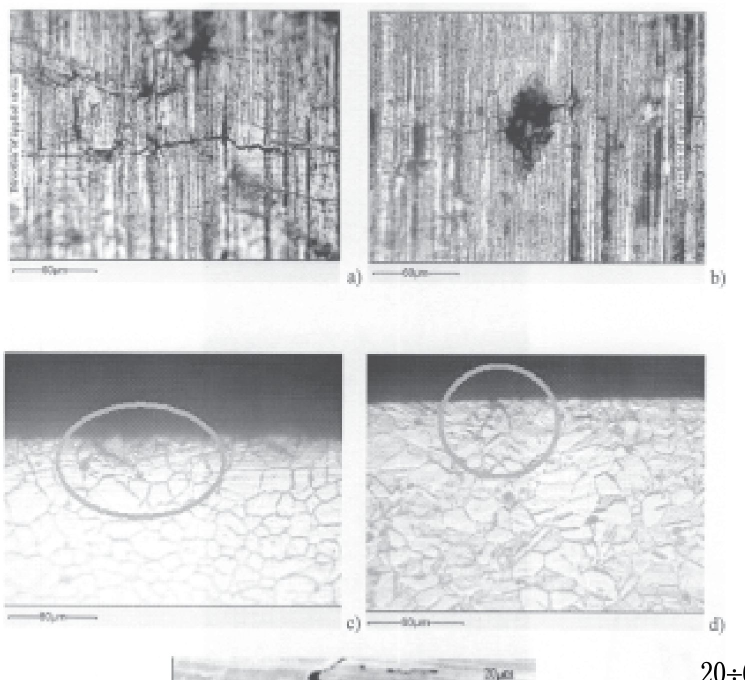
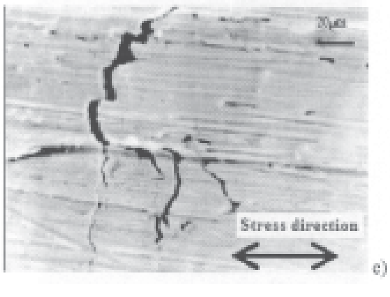



Fig.5. SCC cracks on external surface of Incoloy 800 samples without mechanical pre-crack (deformation 4.5%), tested by potentiostatic method in 0.33g/L NaCl solution, at 85$^{0}$C, applied potential +500mV: a) propagated in the wall of sample; b) started from a pit; c) intergranular initiation; d) transgranular initiation (SEM image x300)




concentration of the testing solution determines the increasing of SCC length: its values were 60÷100µm in the case of samples tested in 0.33g/L NaCl solution and 20÷60µm in the case of 0.033g/L NaCl solution. As it was expected, the pits that built in the more aggressive solution are larger and more profound.

For the study of samples without mechanical pre-crack, it was applied an electrode potential (+500mV chosen from trans-passive PD curve), and this experiment showed that the SCC cracks are longer, of approximately 120mm (fig.5a). Also, it was observed the presence of many incipient SCC cracks formed at boundary of profound pits (fig.5b). The SEM confirms that these SCC cracks are ramified and deep (fig.5e). The micrographs, obtained in the transversal section of the Incoloy 800 samples without mechanical pre-crack, tested by potentiostatic method,

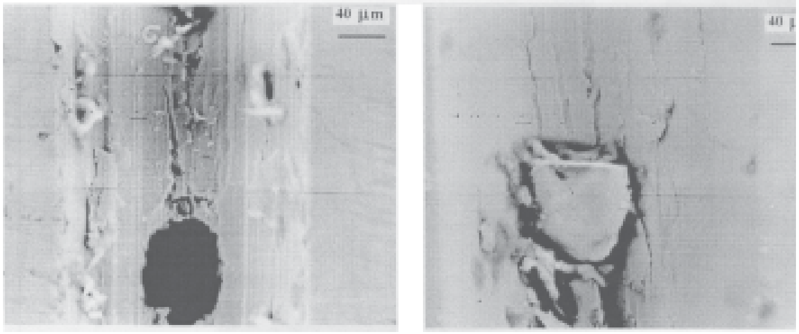



Fig.6. SCC cracks associated with pits in the case of samples tested by dynamic polarization method in 0.33g/L NaCl solution (SEM images x800): a) depth of mechanical pre-crack 100µm (deformation 5%); b) depth of mechanical pre-crack 250µm (deformation 9.4%)

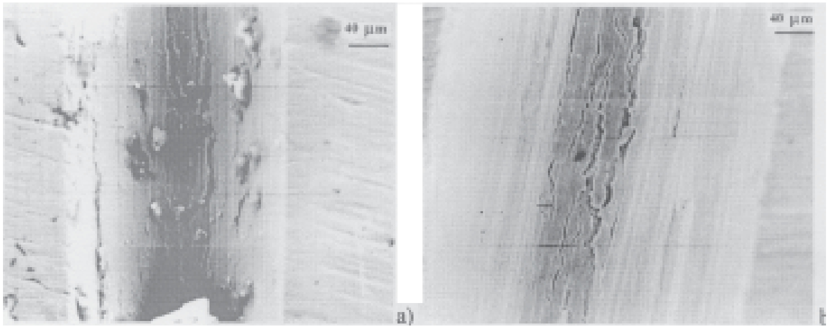



Fig.7. SCC cracks in the case of samples tested by dynamic polarization method in 0.033g/L NaCl solution (SEM images x 800): a) depth of mechanical pre-crack 100µm (deformation 5%); b) depth of mechanical pre-crack 250µm (deformation 9.4%)

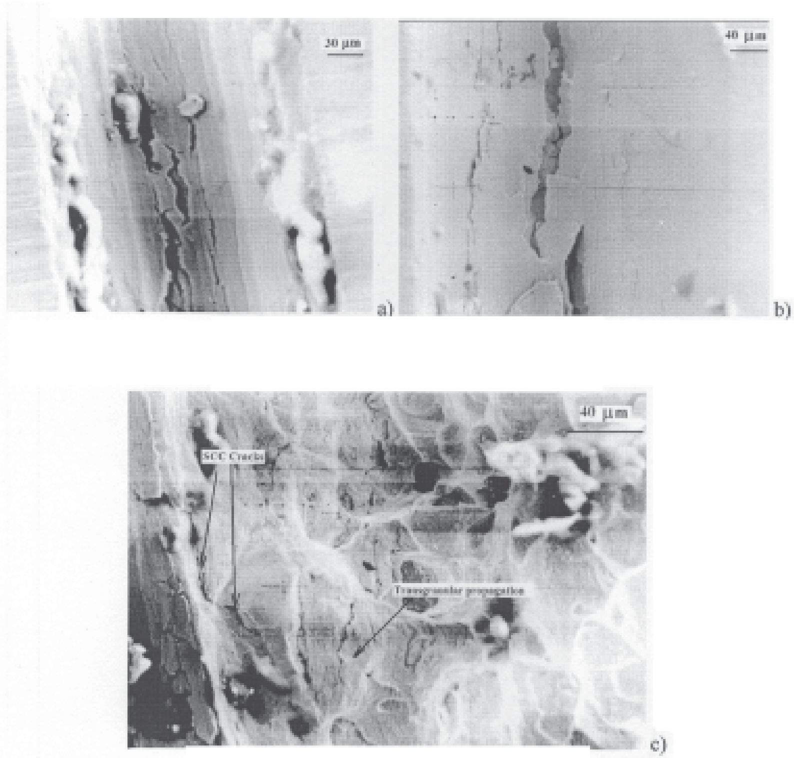



Fig.8. SCC cracks on apex of mechanical pre-crack in the case of samples tested in 0.33g/L NaCl solution at 85$^0$C, polarizing potential +500mVvsSCE (SEM images x800): a) 100µm (deformation 5%); b) 250µm (deformation 9.4%); c) Transgranular propagation of SCC cracks for 9.4% deformation (SEM image x300)

showed that the SCC cracks start at grain boundary when they are not associated with a pit, and continue to propagate trans-granular (fig.5c). The initiation and propagation of the SCC crack are trans-granular, when the crack starts from a pit (fig.5d). The propagation depth is between 30µm and 50µm.

The SEM images captured inside of mechanical pre-crack of the samples tested by potentiodynamic method have put in evidence that SCC cracks appear at the highest point of the mechanical pre-crack. The SCC cracks are always associated with pits in the case of the samples tested in concentrated NaCl solution (fig.6.), while in the case of the samples tested in 0.033g/l NaCl solution the SCC cracks are initiated in the absence of pits (fig.7). In the last case, the augmentation of local deformation implies the increasing of cracks number.

The enforced of potential of +500mVvsSCE, established from trans-passive region of PD curves, determine the occurrence of very deep SCC cracks in the both cases: samples with mechanical pre-crack depth 100µm and, respective 250µm (fig. 8a and 8b). The breakage surface of one sample with a mechanical pre-crack depth of 250µm was analyzed by scanning electron microscopy. It has been observed the breakage morphology characteristic to the trans-granular propagation – the cracks propagate through a grain of a “fan” form – and the presence of SCC cracks that transverse the grains (fig. 8c).

*Stress intensity factor*

Considering that the pits are preferential sites for the initiation of the SCC cracks, it was calculated the stress intensity factor along of one pit by using the dedicated software FEA-Crack for fracture mechanics.

In order to achieve this, it was taken into account the average dimensions corresponding to the pits formed on the surface of the samples tested by potentiodynamic method in 0.33g/L NaCl solution: the average length of the

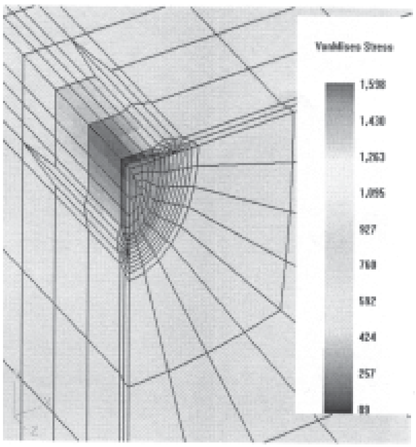


Fig.9. Stress distribution at T=20$^0$C along of border of one pit simulated such as semi-elliptical pre-crack with followed dimension: 2c=0.08mm; a=0.60mm

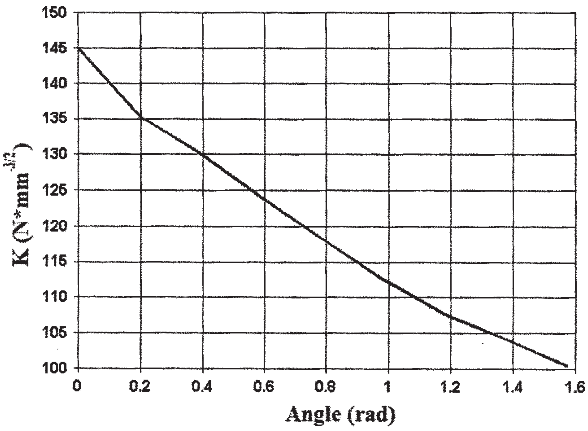



Fig. 10. Evolution of stress intensity factor along of pit border ($K_{Imax}$ =4.58 MPa·m$^{-1/2}$)

pits was 80μm, and the average depth was of 60μm. In the computations it was modeled an elliptical crack with the following dimensions $2c$=0.08mm, and $a$=0.06mm. For the computations, the values for Poisson coefficient (ν) and Young modulus (E) corresponding to the Incoloy 800 alloy (E=196GPa, ν=0.3) were used. Also, the value of applied stress in circumferential direction used was σ=579MPa, such as it resulted from the estimation made using ANSYS code.

The distribution of Von Misses stress along the front of one pit is presented in figure 9, while figure 10 shows the evolution of stress intensity factor. It can be observed that the maximum value of the stress intensity factor is on the border of the pit. This fact is in agreement with the experimental results related above. The maximum value of stress intensity factor was calculated as $K_{Imax}$=145N·mm$^{-3/2}$=4.58MPa·m$^{-1/2}$. This value may be considered the threshold value of stress intensity factor above which the SCC mechanism manifests in the chlorinate environment.

## Conclusions

The value of local deformation is the determining parameter influencing the SCC behaviour of Incoloy 800 in chlorinated environment.

The accelerated tests results show that the increase in the $Cl^-$ concentration in the testing solution involves an increase in the stress corrosion susceptibility of Incoloy 800 alloy. Also, the scanning electron microscopy images demonstrated that the SCC cracks are always associated with pits in more concentrated testing solutions (0.33g/L NaCl). On the contrary, in the case of the samples tested in 0.033g/L NaCl solution it was observed in most cases that the SCC cracks did not start from one pit.

When the SCC cracks start from one pit, the initiation of these cracks is transgranular, while the SCC cracks start intergranular in the absence of the pit. In the last case, the precipitates and inclusions are at grain boundary and act as preferential places for the SCC cracks initiation. However, the propagation of SCC cracks is transgranular in both cases.

Taking into account that the pits may represent considerable initiation points for the SCC cracks in chlorinated environment, it was calculated the evolution of the stress intensity factor along one pit border. In the presented testing conditions, the threshold value for the stress intensity factor was $K_{Imax}$=145N·mm$^{-3/2}$= 4.58 MPa·m$^{-1/2}$. By means of FEA performed with FEA-Crack software this value is achieved at the border of the pit that is in correlation with the experimental results.

## References


1. ANDRESEN P., SHACK W.J., SCC in Acidic, Neutral and Alkaline Environments, Int. Conf. Control of Corrosion on the Secondary Side of *** Steam Generator, Meeting "Improving the Understanding and Control of the Secondary Side of Steam Generators", Virginia, USA, 1995
2. GONZALES F., SPEKKENS P., Nuclear J. of Canada, no 1-2, 1986, p.129
3. WANG R.C., PAN C., TSAI C.H., Nucl. Technol., 94, 1991, p.1
4. HWANG I.S, PARK I.G., Corrosion, 55, No 6, 1999, p. 616
5. GARAUD Y.S., Issues and Modeling Concepts for Assessment of Local Corrosion on the Secondary Side of Steam Generators, Int. Conf. Control of Corrosion on the Secondary Side of Steam Generator, Meeting "Improving the Understanding and Control of the Secondary Side of Steam Generators", Virginia, USA, 1995
6. ***, Corrosion of Metals and Alloys. Stress Corrosion Testing, SR EN ISO 7539-5. Part 5 – Preparation and Use of C-ring Specimens,1996
7. KAWAMURA H., HIRANO H., KOIKE M., SUDA M., Corrosion, 58, No 11, 2002, p. 941
8. DINU A., RADULESCU M., POPA L., The influence of the mechanical state on the stress corrosion cracking initiation in the case of Incoloy-800 alloy in caustic environment", Int. Symp. on nuclear energy: Nuclear power - a new challenge, Bucharest, Romania, 2007
9. MICU F., CERLINCA L., ENGI E.A., Chemical Technical Section Cernavoda NPP, 1995



Manuscript received: 18.09.2013