

COMMISSARIAT A L'ENERGIE ATOMIQUE

FR8903924

CENTRE D'ETUDES NUCLEAIRES DE SACLAY

CEA-CONF --9877

Service de Documentation

F91191 GIF SUR YVETTE CEDEX

M2

STRESS CORROSION CRACKING OF NICKEL BASE ALLOYS CHARACTERIZATION  
AND PREDICTION

SANTARINI G.- PINARD-LEGRY G.  
CEA Centre d'Etudes Nucleaires de Fontenay-aux-Roses, 92 (FR). Dept.  
de Chimie Appliquee et d'Etudes Analytiques

Communication présentée à : EUROCORR'88: Symposium on Corrosion  
Brighton (UK)  
3-5 Oct 1988

CORROSION UK/ EURO CORR '88.

Brighlon, England

3 - 5 / 10 / 88

S36



STRESS CORROSION CRACKING OF NICKEL BASE ALLOYS : CHARACTERIZATION AND PREDICTION

G. Santarini, G. Pinard-Legry  
Commissariat à l'Energie Atomique, IRDI/DERDCA/DCAEA/SCECF,  
Centre d'Etudes Nucléaires, B.P. 6, 92265 Fontenay-aux-Roses Cedex, France

ABSTRACT

For many years, studies have been carried out in several laboratories to characterize the IGSCC (Intergranular Stress Corrosion Cracking) behaviour of nickel base alloys in aqueous environments. For their relative shortness, CERTs (Constant Extension Rate Tests) have been extensively used, especially at the Corrosion Department of the CEA. However, up to recently, the results obtained with this method remained qualitative. This paper presents a first approach to a quantitative interpretation of CERT results. The basic datum used is the crack trace depth distribution determined on a specimen section at the end of a CERT. It is shown that this information can be used for the calculation of initiation and growth parameters which quantitatively characterize IGSCC phenomenon. Moreover, the rationale proposed should lead to the determination of intrinsic cracking parameters, and so, to in-service behaviour prediction.

1 - INTRODUCTION

The austenitic Fe-Cr-Ni alloys are widely used in light water nuclear reactors for their good resistance to generalized corrosion. However, when their nickel content is not high enough, these alloys are known to be subject to transgranular cracking in media containing chlorides and oxygen. This consideration led several manufacturers to settle on nickel base alloys, especially for sensitive components such as the Steam Generators (SG) of Pressurized Water Reactors (PWR). Alloy 600, containing about 75 per cent nickel and 15 per cent chromium is now the most generally used, all over the world, for SG tubing.

Nevertheless, a continuously increasing number of localized corrosion problems demonstrated that this choice was probably not the best one. Among the phenomena involved, a particularly pervasive one appeared to be the Intergranular Stress Corrosion Cracking (IGSCC) of Alloy 600 on the inner (primary) side of the tubes [1] to [7]. Such a cracking was initially

rather surprising, considering the apparently low aggressiveness of primary water.

After a brief historical survey, this paper will emphasize the need of a modelization and present a first approach to quantitative characterization and prediction of nickel base alloy IGSCC.

## 2 - BRIEF HISTORICAL SURVEY

### 2.1 - First Laboratory Tests

In fact, as early as 1959, H. Coriou, head, at that time, of the Corrosion Department of the Commissariat à l'Energie Atomique (CEA) in France, pointed out the risk of cracking of Alloy 600 when stressed in pure water, at high temperature [8] to [10]. This assumption was based on the results of tests performed on plates bent slightly above the yield strength. They showed that, at 350°C, this alloy could crack after a few months of exposure. However, these results gave rise to much controversy, the phenomenon being, at best, considered as a laboratory curiosity rather than a real threat to plants.

### 2.2 - Cracking in Plants: "Coriou Effect"

Since the early 70's and up to now, number of leakages, eddy current indications and tube extractions have confirmed the actuality of the phenomenon in operating nuclear power plants and, nowadays, the Primary Water Stress Corrosion Cracking (PWSCC) or "Coriou effect" of nickel base alloys is regarded as one of the most worrying problems concerning plant durability. Alloy 600 cracking occurs in regions submitted to relatively high stresses such as transitions from bent to straight portions of small radius U-bends, or roll transitions at the tube-to-tubesheet joints. The slow recognition of the risk, during the early years, is probably due to some characteristics of this type of cracking making it difficult to reproduce in laboratory:

- a great variability in sensitivities is observed from heat to heat;
- the initiation time may be very long;
- this cracking usually needs very high tensile stresses.

It has to be noted that PWSCC is a generic problem with high-nickel austenitic alloys. It is not confined to SG, but affects also the internal structures of the vessels: bolts and tube guide pins made of precipitation-hardened high-nickel alloys.

### 2.3 - Test Methods

Facing the growing industrial concern related to PWSCC, number of laboratory studies have been carried out all over the world. They are, mainly, purely empirical studies which can lead to rather satisfactory behaviour characterization, but in conditions usually completely different from those of the field. Reasonable rankings can be obtained but predictions remain hazardous. The tests used for these characterizations may be constant deformation tests (C-rings, U-bends, reverse U-bends, etc.), constant load tests or, in some cases, Constant Extension Rate Tests (CERTs).

This last type of test deserves special attention since, although it is as global as the other ones, it is relatively short and seems likely to provide more information [11] to [15]. CERTs have been extensively used, for

3

many years, at the Corrosion Department of the CEA, with specially designed autoclaves (Fig. 1). An originality of these CEA devices consists in their particular loading system: the tensile specimen hangs on the lid and its straining is obtained by pulling down its lower head. This specimen is, most frequently, machined from a tube (Fig. 2). In most cases, SCC occurrence is not clearly revealed by modifications in the stress-strain curves. So we have had to examine carefully the morphology of cracked specimens after the tests. Up to recently, these observations led to only qualitative rankings, but, as it will be presented farther on, a method for extracting much more information from these morphological observations is presently under development.

#### 2.4 - Global Characterizations. Influence of Various Parameters [1]

With the methods referred to in the previous section, a screening of the overall influences of various parameters was obtained, as shortly summarized below.

Influence of alloy composition. PWSCC resistance is improved by decreasing nickel content. Fe-Cr-Ni alloys with nickel contents between 20 and 65% such as Incoloy 800 (30% Ni, 20% Cr) and Alloy 690 (60% Ni, 30% Cr) seem to be completely immune. Alloy 690 is now adopted for SG tubing of new plants.

Influence of microstructure. The most resistant structures appear to be those exhibiting semicontinuous intergranular carbide precipitation with no intragranular carbides. These structures are obtained with alloys containing between about 0.02 and 0.03% carbon, annealed at temperatures higher than 1000°C, then thermally treated at 700°C during at least 12 hours.

Influence of stress: A decreasing power law dependence of the time-to-rupture on the applied stress has been proposed for constant load tests, the suggested exponent being about -4. This relation has to be considered very cautiously, since such a global value as time-to-rupture in a particular test may result from several elementary steps, thus depending on the type of test.

Influence of environment and temperature: Some results seem to indicate that primary water is rather less aggressive than pure water, but these results are in disagreement with others. Hydrogen, at a partial pressure of a few bars, is deleterious, but its influence as a function of its partial pressure is still unclear. More generally, studies on the influence of environmental factors often lead to puzzling results. Here again, the situation is probably due, in large part, to the use of too global parameters, the environmental factors influencing differently each elementary step. Concerning the role of temperature, apparent activation energies would lie between 125 and 200 kJ.mol<sup>-1</sup> from laboratory tests.

### 3 - NEED OF MODELIZATION. MECHANISTIC MODELS AND PHENOMENOLOGICAL MODELS

The considerations above seem to indicate that characterizations using only global parameters already reached their ultimate limits. Now, any progress in understanding the respective influences of environmental factors and in behaviour prediction will probably need modelization. However, it must be clear that this theoretical way may present very different kinds of approaches, with different kinds of difficulties. Schematically, the models

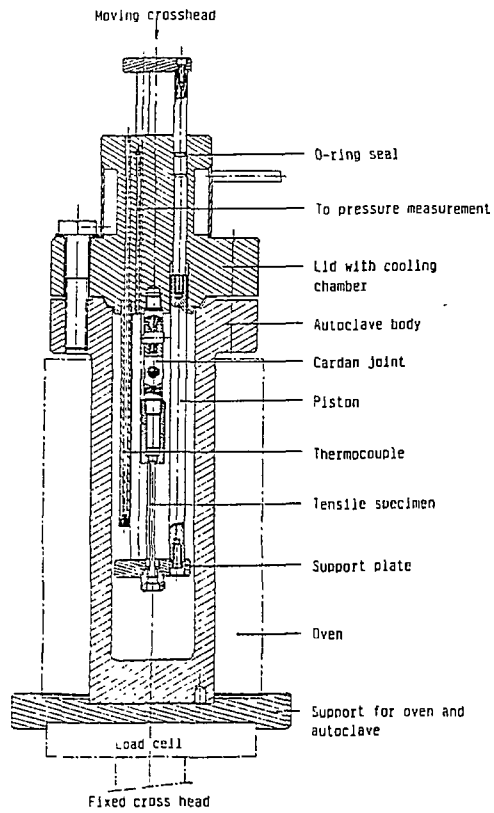


Figure 1: CEA autoclave for constant extension rate tests

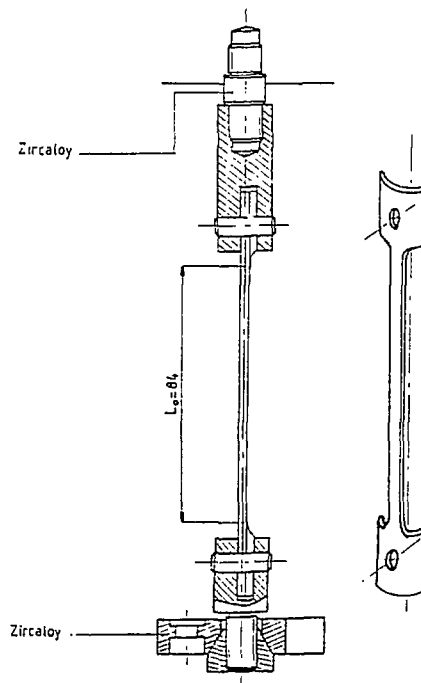


Figure 2: Tensile specimen for constant extension rate test

can be considered as distributed among two categories: the mechanistic approach and the phenomenological approach.

In the first one lie all the efforts to better understand the roles of the (relatively) elementary steps in the overall IGSCC phenomenon. It includes mainly models on hydrogen embrittlement and on film-rupture anodic dissolution. In spite of their fundamental interest, these models are not very likely to provide, reasonably soon, usable in-service predictions. They come up against the complexity of numerous interconnected steps; data are often missing and predictions based only on studies of the mechanism would require numerous specific experiments.

The second approach is nowadays gaining support [16]. It consists in semi-empirical modeling with limited reference to mechanistic considerations. The study presented in the following sections lies in this category: its aim is to provide a general method for the complete characterization and ultimately for the prediction of IGSCC behaviour, by simply analyzing the morphological information present in the results of CERTs. This presentation will be limited to general trends; the method will be thoroughly explained and commented in further publications.

#### 4 - IN SEARCH OF A MORPHOLOGICAL MODEL

##### 4.1 - Context. Chemical Kinetics and Morphological Kinetics

The work is part a of wider one undertaken a few years ago in the Corrosion Department of the CEA to analyse the relations between morphology and kinetics at interfaces. It includes studies of morphological interfacial instabilities in their global [17] and also local aspects (pitting, SCC, etc.). The basic idea is to exploit the reciprocity between chemical kinetics and morphological kinetics. The conditions related to chemical or physico-chemical kinetics at an interface determine the evolution of the interfacial shape, but, reciprocally, this morphological evolution gives information on chemical (or physico-chemical) kinetics. This last half of the statement is rarely considered, though it could lead to very fruitful developments. Applied to local instabilities, it means that crack distribution, as a function of time, gives access to an information on crack initiation, crack growth, and even on the mechanisms of these steps [18].

##### 4.2 - Basic Experimental Datum: The Crack Trace Depth Distribution

Cutting a specimen along a symmetry plane (parallel to the direction of stress) at the end of a CERT of duration T and measuring the depths of the crack traces found in this plane gives access to the crack trace depth distribution. This distribution may be conveniently characterized by the function  $N(\ell, T)$ , i.e. the number of crack traces of depth higher than  $\ell$  present on a calibrated specimen length  $L_0$ . This function is the primary experimental datum which will be used for the determination of cracking parameters. A more direct representation would have been obtained, for example, with a function  $M(\ell, T)$ , i.e. the number of cracks of depth higher than  $\ell$  present on a calibrated specimen length  $L_0$ , per width unit. Unfortunately, this function  $M(\ell, T)$  is not easily accessible experimentally, but it can be proved [18] that, if the cracks are assumed to be triangular, with a constant ratio  $\alpha$  between their half width and their depth, then  $M(\ell, T)$  and  $N(\ell, T)$  are simply linked by derivation:

$$M(\ell, T) = \frac{-1}{2\alpha} \frac{\partial N(\ell, T)}{\partial \ell} \quad (1)$$

#### 4.3 - Characteristic Cracking Functions: $p(t)$ , $v(\ell, t)$

Initiation: If  $\lambda_0$  is the fraction of the total number of surface grain boundaries available for cracking ( $0 < \lambda_0 \leq 1$ ) or, in other words, the fraction of surface grain boundaries that are liable to behave as actual initiation sites, and  $p$  the initiation probability on an available grain boundary per unit of time, the number of initiating cracks, during  $dt$ , on a longitudinal surface band of length  $L_0$  and of width unity is  $p \frac{\lambda_0 L_0}{\epsilon_0^2} dt$ ,  $\epsilon_0$

being the mean grain size. This expression is valid as long as the grain boundary saturation effect for crack initiation is neglected, which means that the number of initiation sites is assumed to remain approximately constant during the entire test.

The probability so defined is analogous to a radioactive disintegration probability, but it must be pointed out that, in the general case of a CERT,  $p$  is a function of the time  $t$  from the start of this CERT:  $p(t)$ . The primitive  $P(t) = \int_0^t p(t) dt$  is the fraction of available surface grain boundaries that, at time  $t$ , have actually initiated cracks ( $0 < P \leq 1$ ).

Growth: In the general case, the growth rate  $v$  of a crack in a CERT can always be considered as a function of two parameters:  $t$ , the time from the start of the test, and  $\ell$ , the depth of the crack at time  $t$ :  $v(\ell, t)$ .

#### 4.4 - Relations between Crack Trace Depth Distribution and Characteristic Cracking Functions

The  $M(\ell, T)$  cracks that, at the final time  $T$  of a CERT, are of depths higher than  $\ell$ , are those which were initiated at times between  $t = 0$  and  $t = t_a$ ,  $t_a$  being a function of  $\ell$  and  $T$ :  $t_a(\ell, T)$ . At this time  $t_a$ , the total number of cracks, on a specimen length  $L_0$  and per width unit, was (see section 4.3):

$$\frac{\lambda_0 L_0}{\epsilon_0^2} \int_0^{t_a} p(t) dt.$$

Hence:

$$P[t_a(\ell, T)] = \frac{\epsilon_0^2}{\lambda_0 L_0} M(\ell, T) \quad (2)$$

and, if the cracks are assumed to be triangular [relation (1)]:

$$P[t_a(\ell, T)] = \frac{-\epsilon_0^2}{2 \alpha \lambda_0 L_0} \frac{\partial N(\ell, T)}{\partial \ell}. \quad \text{As a consequence, since the initiation time}$$

of a crack that at final time  $T$  has a depth of zero, is  $t_a(0, T) = T$ , we

$$\text{have: } P(T) = \frac{-\epsilon_0^2}{2 \alpha \lambda_0 L_0} \frac{\partial N(0, T)}{\partial \ell}. \quad \text{Function } P \text{ is therefore directly related to}$$

the slope of the graph of  $N(\ell, T)$  for  $\ell$  equal to zero. Hence, by derivation:

$$p(T) = \frac{-\epsilon_0^2}{2 \alpha \lambda_0 L_0} \frac{\partial^2 N(0, T)}{\partial \ell \partial T} \quad (3)$$

Moreover, the cracks that, at final time T of a CERT, have reached a depth  $\ell$ , would have reached, in another CERT interrupted at time T + dT, a depth  $\ell + v(\ell, T) dT$ . Their initiation time  $t_a$  remaining the same, we have:  $t_a[\ell + v(\ell, T)dT, T + dT] = t_a[\ell, T]$ ; hence:

$$\frac{\partial t_a(\ell, T)}{\partial \ell} v(\ell, T) dT + \frac{\partial t_a(\ell, T)}{\partial T} dT = 0 \quad v(\ell, T) = \frac{-\frac{\partial t_a(\ell, T)}{\partial T}}{\frac{\partial t_a(\ell, T)}{\partial \ell}}$$

and, with relation (2):  $v(\ell, T) = \frac{-\frac{\partial M(\ell, T)}{\partial T}}{\frac{\partial M(\ell, T)}{\partial \ell}}$

Finally, with triangular cracks [equation (1)], we obtain:

$$v(\ell, T) = \frac{-\frac{\partial^2 N}{\partial \ell \partial T}}{\frac{\partial^2 N}{\partial \ell^2}} \quad (4)$$

Relations (3) and (4) are the keystone of this theoretical work. They show the existence of a one-to-one relation between the function  $N(\ell, T)$  experimentally determined in a series of interrupted CERTs (all performed at the same extension rate) and the pair of functions  $p(t)$ ,  $v(\ell, t)$  characterizing the cracking behaviour in any of these CERTs. The principle of the proposed method is to use equations (3) and (4) (or other similar expressions, if the cracks cannot be assumed to be triangular, but are rather rectangular or semicircular) for obtaining  $p(t)$  and  $v(\ell, t)$  from  $N(\ell, t)$ . More details concerning the mathematical methods needed will be given in further papers.

It is remarkable that the forms obtained for functions  $p(t)$  and  $v(\ell, t)$  give, without any mechanistic consideration, indications for an initial screening of the various classes of mechanistic models which are a priori possible.

Figure 3 shows examples of  $N(\ell, T)$  functions experimentally determined with mill annealed Alloy 600 tubes strained at a constant extension rate of  $2.5 \times 10^{-7} s^{-1}$  in primary water (with about  $10^{-2}$  mole.kg $^{-1}$  hydrogen) at 360°C. A first application of the proposed method to this case leads to the following interpretation:  $p$  is a power law of time;  $v$  is a function of  $\ell$  only, with a constant value of about 0.4  $\mu m \cdot h^{-1}$  for  $\ell$  lower than a critical value, and again a constant value, but of about 5  $\mu m \cdot h^{-1}$ , for  $\ell$  higher than this critical value. This critical value is of about 60  $\mu m$ . This interpretation has yet to be confirmed and refined.

## 5 - QUANTITATIVE CHARACTERIZATION AND PREDICTION

### 5.1 - Extrinsic Parameters and Intrinsic Parameters

In the expressions of  $p(t)$  and  $v(\ell, t)$ , the parameters independent on  $\ell$  and on  $t$  are extrinsic cracking parameters: they characterize cracking behaviour, but only in the conditions of a CERT performed at a given value of



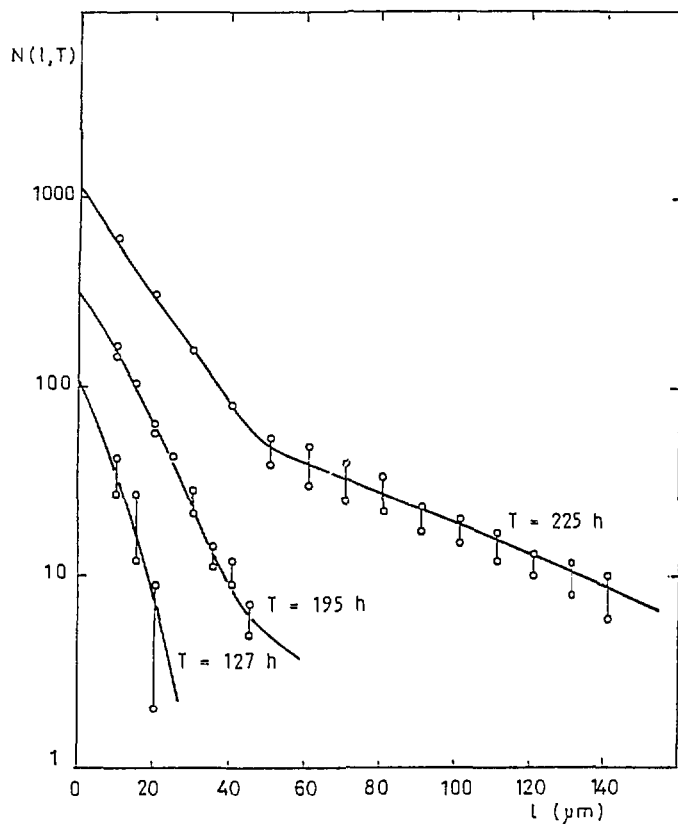


Figure 3: Interrupted CERTs (extension rate:  $2.5 \times 10^{-7} \text{ s}^{-1}$ )  
Some crack trace depth distributions ( $L_0 = 84 \text{ mm}$ )  
o Experimental values  
- Calculated curves

extension rate. Determining the dependence of these parameters on extension rate leads to more general cracking parameters, characterizing cracking behaviour in any CERT. Intrinsic cracking parameters are only obtained when  $p$  and  $v$  are expressed as functions of factors independent on the type of test, such as stress, or strain rate, or crack number, etc. Then only, they can be used for behaviour prediction under any mechanical solicitation, and not only under that of a CERT.

## 5.2 - Access to Intrinsic Cracking Parameters

Quantitative cracking characterization needn't to reach the level of intrinsic parameters. The use of extrinsic cracking parameters would already be a great improvement in studies on the effects of various environmental parameters (see section 2.4). However, industrial need of prediction methods justifies the efforts in the ultimate upgrade. The difficulty here is that the last step is no longer a mere deduction as was the one using equations (3) and (4): the time  $t$  in a CERT cannot be unambiguously interpreted in terms of stress, or strain, or crack number, etc., without extra tests. The various possibilities have to be tested independently of CERTs, by means, for example, of constant load tests. This work is presently under way at the CEA, for Alloy 600; it will be published later on. An important point is that, once this last "grid", for deciphering the function  $N(l, T)$ , is found, only one CERT per material-environment couple will remain strictly

necessary for the determination of intrinsic cracking parameters, and thus for complete behaviour characterization and prediction.

## 6 - CONCLUSION

It can be surprising to see that, after almost thirty years, and in spite of its involvement in very worrying industrial concerns, "Coriou effect" is still so poorly understood and predicted. The complexity of the material-environment couple in question is certainly a reason, as in many cases of corrosion encountered in industrial plants, but the main cause of this situation is probably due to the general lack of enough work in the wide gap between fundamental ("academic") research and purely empirical applied studies. The observation scale is usually too large or too small. The proposed method lies in one of the intermediate ways. It has still to be improved, but seems already liable to provide a useful tool for both following purposes:

- to face the industrial problem with accurate characterizations and predictions;
- to contribute to the effort in more fundamental research, by providing a general method for the screening of possible mechanistic models.

## REFERENCES

- [1] Pinard-Legry, G. Journée SFEN "Tubes de générateurs de vapeur des REP. Corrosion en milieu primaire. Prévention et remèdes". Paris, December 1986, Société Française d'Energie Nucléaire
- [2] Bandy, R., Van Rooyen, D. Corrosion, Vol 40, N° 8, p 425 (1984)
- [3] Economy, G., Jacko, R.J. Corrosion/86, Paper N° 250, Houston, Texas, March 1986, National Association of Corrosion Engineers
- [4] Bandy, R., Van Rooyen, D. J. Materials for Energy Systems, Vol 7, N° 3, p 237 (1985)
- [5] Steam Generator Owners Group and Electric Power Research Institute "Steam generator reference book" EPRI, 1985, Palo Alto CA
- [6] Owens, C.M. Materials Performance, Vol 25, N° 1, p 49 (1986)
- [7] Economy, G., Jacko, R.J., Pement, F.W. Corrosion, Vol 43, N° 12, p 727 (1987)
- [8] Coriou, H. et al. 3ème Colloque de Métallurgie, Saclay (France), June/July 1959, N. Holland Publishing, Amsterdam, 1960, p 161
- [9] Blanchet, J., Coriou, H., Grall, L., Mahieu, C., Otter, C., Turluer, G. J. Nucl. Mater., Vol 55, p 187 (1975)
- [10] Coriou, H., Grall, L., Mahieu, C., Pelras, M. Corrosion, Vol 22, N° 10, p 280 (1966)
- [11] American Society for Testing and Materials, "Stress corrosion cracking - The slow strain rate technique" ASTM special technical publication 665, Philadelphia, Pa., 1979, G.M. Ugiansky, J.M. Payer, editors
- [12] Capener, E.L., Richman, R.H. Corrosion, Vol 42, N° 8 (1986)
- [13] Parkins, R.N. Corrosion, Vol 43, N° 3 (1987)
- [14] Totsuka, N., Lunarska, E., Cragolino, G., Szklarska-Smialowska, Z. Scripta Met., Vol 20, p 1035 (1986)
- [15] Congleton, J., Parkins, R.N. Nuclear Engineering and Design, Vol 103, p 301 (1987)
- [16] Garud, Y.S., Mc Ilree, A.R. Corrosion, Vol 42, N° 2, p 99 (1986)
- [17] Santarini, G. Journal de Chimie Physique, Vol 83, N° 1, p 49 and N° 4, p 329 (1985)
- [18] Santarini, G. Corrosion, to be published