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THE IMPORTANCE OF THE STRAIN RATE AND CREEP ON THE STRESS CORROSION CRACKING MECHANISMS AND MODELS

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ABSTRACT

Stress corrosion cracking is a nuclear, power, petrochemical, and other industries equipments and components (like pressure vessels, nozzles, tubes, accessories) life degradation mode, involving fragile fracture. The stress corrosion cracking failures can produce serious accidents, and incidents which can put on risk the safety, reliability, and efficiency of many plants. These failures are of very complex prediction. The stress corrosion cracking mechanisms are based on three kinds of factors: microstructural, mechanical and environmental. Concerning the mechanical factors, various authors prefer to consider the crack tip strain rate rather than stress, as a decisive factor which contributes to the process: this parameter is directly influenced by the creep strain rate of the material. Based on two KAPL-Knolls Atomic Power Laboratory experimental studies in SSRT (slow strain rate test) and CL (constant load) test, for prediction of primary water stress corrosion cracking (PWSCC) in nickel based alloys, it has done a data compilation of the film rupture mechanism parameters, for modeling PWSCC of Alloy 600 and discussed the importance of the strain rate and the creep on the stress corrosion cracking mechanisms and models. As derived from this study, a simple theoretical model is proposed, and it is showed that the crack growth rate (CGR) estimated with Brazilian tests results with Alloy 600 in SSRT, are according with the KAPL ones and other published literature.

1. INTRODUCTION

The stress corrosion cracking (SCC) is a very intricate degradation process, and depends upon many parameters [1],[2]. These are classified in microstructural, mechanical and environmental [3].

The mechanical factors are: (1) applied and residual stresses: these stresses and geometry can be summarized as stress intensity K (optionally, can be used strain and strain rate which can be also described related to stresses). The microstructural factors are: (2) grain boundary chemistry and segregation; (3) thermal treatment which can causes intragranular and intergranular metallic carbide distribution; (4) grain size and cold work or plastic deformation - the two last ones fix the yield strength: these factors can be described as A in Figure 1. The environmental factors are: (5) temperature T; (6) activity of $[H]^+$ or pH; (7) solution or water chemistry; (8) inhibitors or pollutants in solution: these two last ones can be described as [*x*] in Figure 1; (9) electrochemical and corrosion potentials E and E_o; (10) partial pressure of hydrogen which reflects on potential [3]. This environmental cracking susceptibility can be expressed as showed in Figure 1[4].

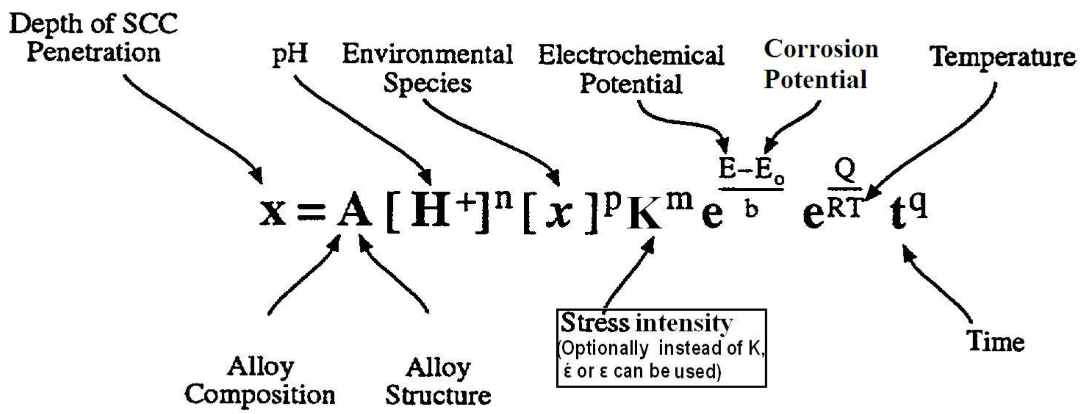


Figure 1. General phenomenological relationship for SCC process depending on many parameters; b, m, n, p, q are adjusted constants, Q the thermal activation energy, and R the universal gas constant. Adapted from [4].

Therefore there are some models to give to SCC mechanisms a mathematic description. In this paper, one considers a SCC case in nickel superalloys (alloys 600 and 182) and stainless steel 304, at high temperature (280°C to 360°C) water to LWR (light water reactors): PWR (pressurized water reactor) and BWR (boiler water reactor). For these cases, the main applicable models are the slip-step dissolution and film rupture model as developed by Andresen and Ford [5], the internal oxidation mechanism of Scott and Le Calvar [6], the coupled environment fracture model of Macdonald and Urquidi-Macdonald [7], numerical models of Rebak and Szklarska-Smialowska, and others which can be applied in this case [3].

One of the most important and used, the slip-step dissolution and film rupture model [5], is based on the oxide passive film´ s electrochemical dissolution and repair cycle driven by the crack tip strain rate. This is caused by strain rate applied, produced on SSRT (slow strain rate test), or caused by applied and residual local stresses. Further, there is the local creep strain rate due to material to be added.

The objective of this paper is to evaluate and to discuss the crack tip strain rate effect on PWSCC of the nickel-alloy 600, including the main contribution of the applied loads and the creep, based on experimental work developed by the KAPL researchers [8], [9] by SSRT and

CL (constant load) tests, and compared with the Brazilian experiments using SSRT. As derived from this study, a simple theoretical model is proposed.

2. THE SLIP-STEP DISSOLUTION AND FILM RUPTURE MODEL

This model is very important and applicable to the stress corrosion cracking (SCC) cases in nickel superalloys (alloys 600 and 182) and stainless steel 304, at high temperature (280^{o}C to 360^{o}C) water to LWR. It has been developed in General Electric Laboratories, mainly as an engineering model to be applicable to supervisory control systems of big rotating machines [5]. It has also been very intensely reviewed, and discussed in the last years, due to its importance and applicability. A very good review can be found in Hall Jr.´ s paper [10].

The slip-step dissolution and film rupture model, based on the oxide passive film´ s electrochemical dissolution and repair cycle driven by the crack tip strain rate (Figure 2 [11]), has its basic model written as equation (1) (adapted from [8]) for a fixed temperature.

$$\mathbf{CGR= (Mi_0t_0/\rho zFt_r)(1/N+1)[N+(t/\ t_0)^{N+1}].(K - K_{th})^n} \tag{1}$$

with: CGR, the crack growth rate [cm/s]; M=atomic weight [g/mole]; ρ=density [g/cm^3]; z=valence [eq/mole]; F= Faraday constant [96485 C/eq]; t_r=time between two film rupture consecutive events [s] with $i(t)=i_0$ for $0 \leq t \leq t_0$ and $i(t)=i_0(t/\ t_0)^N$ for $t \geq t_0$ with i_0 = nude surface current density [A/cm^2]; N= repassivation rate with N<0; K=stress intensity; K_{th} =threshold stress intensity [MPa.m$^{1/2}$]; n=-N.

2.1. Strain Rate rather than Stress

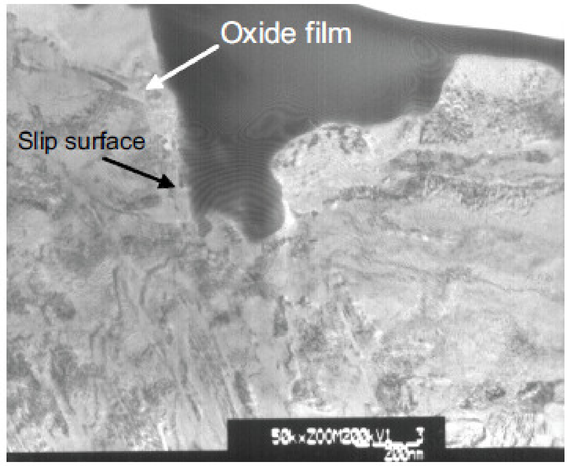
The equation (1) describes adequately the fracture mechanics curve CGR vs. K, but the K member can be replaced according equation (2) [9], for a fixed temperature.

$$\mathbf{CGR\ (crack\ tip) = A.K^{4n`} = A.\acute{\varepsilon}^{\,n`}} \tag{2}$$

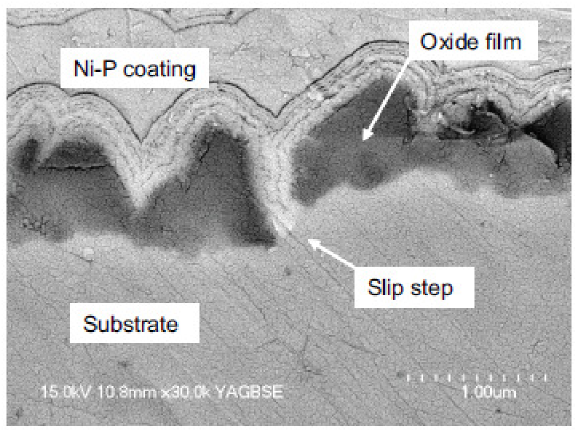
with: A= constant resuming the first to third member of equation (1); n`= repassivation rate; έ=crack tip strain rate.

This transformation between equations (1) to (2) is because some authors [3], [5] prefer to highlight the strain rate rather than the stress influence on SCC process.

So, it can be studied the crack tip strain rate influence. This parameter is constituted by the strain rate applied (produced on SSRT, or caused by applied and residual local stresses), and the creep strain rate contribution.



(a)



(b)

Figure 2. Slip bands details of SCC process: (a) Film structure of surface oxide on test material (austenitic stainless steel). The band width length is about 300 nm; (b) Detail shows a slip step found in a specimen section, where this SCC rupture process can be clearly seen in this step [11].

3. THE KAPL EXPERIMENTS WITH NICKEL SUPERALLOYS

The Knolls Atomic Power Laboratory-KAPL experimental work with nickel superalloys in high temperature water environment, developed on SSRT and CL tests [8], [9], are important to better understand the strain rate and creep strain rate role on stress corrosion cracking of these materials.

The tests were based on a creep apparatus composed by an autoclave, a loading system, and a water circulation system (Figure 3 [12]). The tests by constant load were performed on round bar specimens. The creep strain rate was measured by an external Linear Variable Differential

Transformer (LVDT) attached to the system pull rod. In some tests an internal LVDT provided simultaneous, in-situ measurements of sample displacement. For more details, see reference [12]. Some of the results are very interesting and didactic, as the shown in Figure 7, where can be distinguished the primary and the secondary creep strain rate [8].

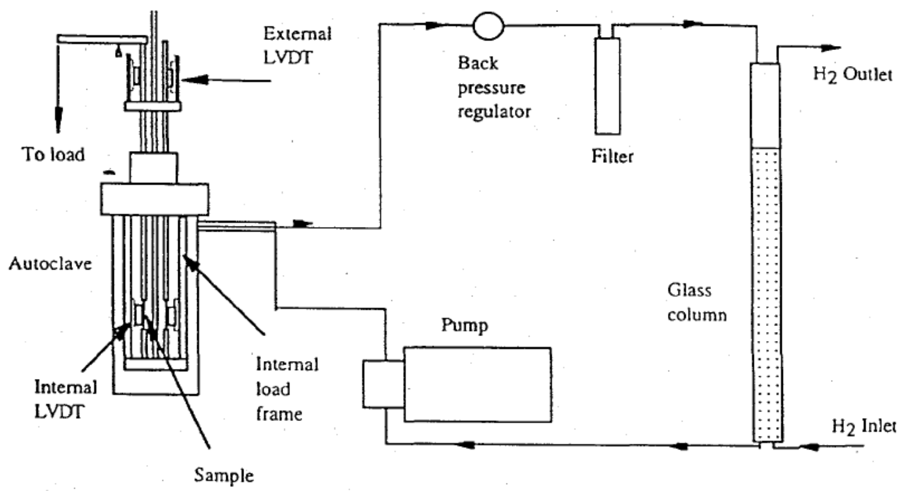


Figure 3. Schematic draw of multiple sample constant loading tests apparatus used on KAPL experimental work [12].

3.1. Main KAPL Results of Experimental Work with Alloy 600

3.1.1. Experimental Data about Alloy 600 (and Alloy 690) Repassivation in the PWSCC Conditions

Concerning Figure 4 (b), each step of mass loss produced additional 3% strain. Based on this test, it was evaluated the slopes of the curves that give the value of N in the model formulation and it was obtained $-0.40 < N_{Alloy600} < -0.42$ and - $0.53 < N_{Alloy690} < -0.56$, which implies a $CGR_{Alloy600}$ ~3.7 to 8.7 $CGR_{Alloy690}$, confirming that the Alloy 690 with almost twice the content of Cr relative to Alloy 600, is much more resistant than this to SCC (see from the graph that the repassivation time of the Alloy 690 is smaller than that of Alloy 600). There is a difference on "n" value when compared Figure 4 (a) with Figure 4 (b).

3.1.2. **Experimental Data about Film Rupture considering the Chromium Effect**

The tests were of the type SSRT at 288 °C in material Ni-9Fe-XCr (Cr content ranging between 4.6 and 41% by weight) with a strain rate of 6 to 12.10^{-5} s^{-1} and with the specimens 50mV anodically polarized with respect to open circuit potential for 24 to 72 hours before straining. The strains were measured on site using an Eddy Current sensor connected to the specimens. These specimens were pre-strained with 20% of cold work for guarantee that the event of rupture of the oxide would occur well before the plastic straining of the specimens.

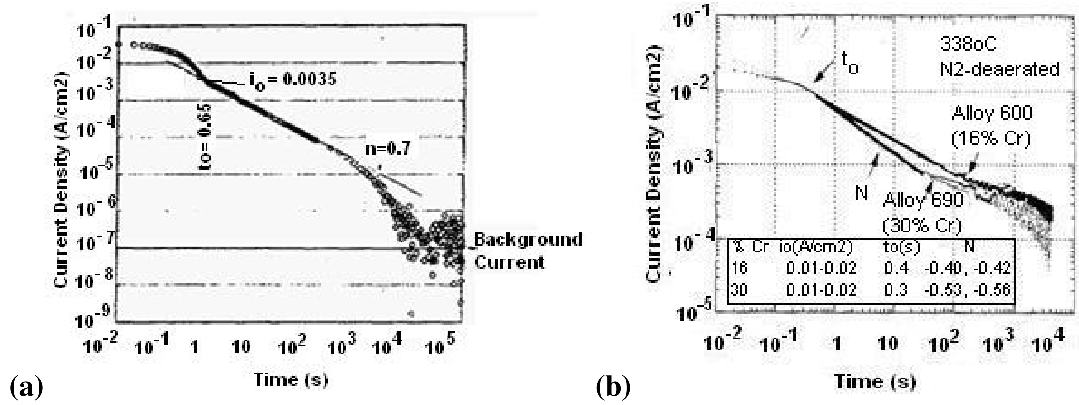


Figure 4. Repassivation of the Alloy 600 in two separate experiments: (a) using a pulse potential of -1500 mV_{SHE} to -711 mV_{SHE} at 288°C (minimum anodic current density on the surface without passive film = 3.5 mA/cm^2) and (b) The same with the test at 338°C [8], [9].

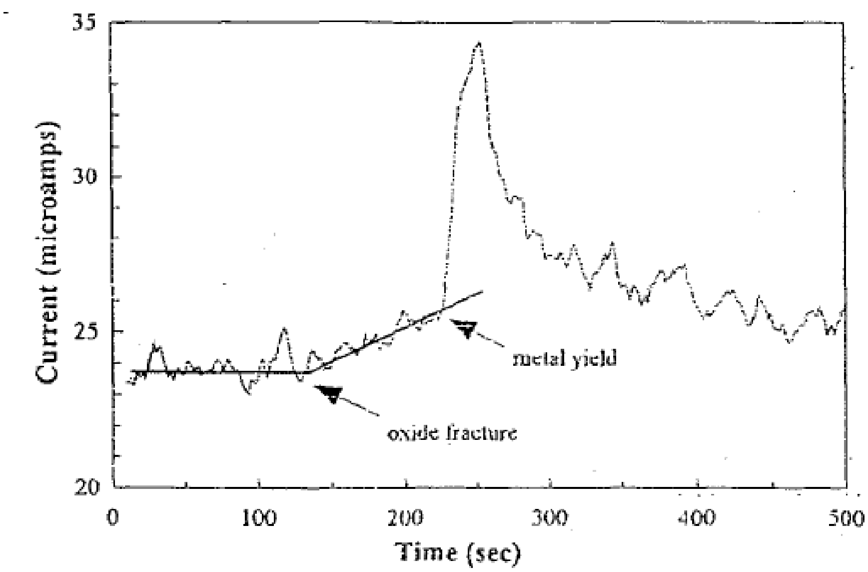


Figure 5. Current plot vs. time of the film rupture test of nickel alloys specimens [8].

In Figure 5, one notes from the lower left, the following steps: (a) basic passivation current before the pre-strain = 24±1μA (b) film rupture after 140s: the current increase after this was attributed to corrosion of metal under the broken oxide layer, (c) metal yield occurs after 230 s, (d) the occurrence in large-scale of slip-steps is indicated by the sudden increase in current from 230 s [8].

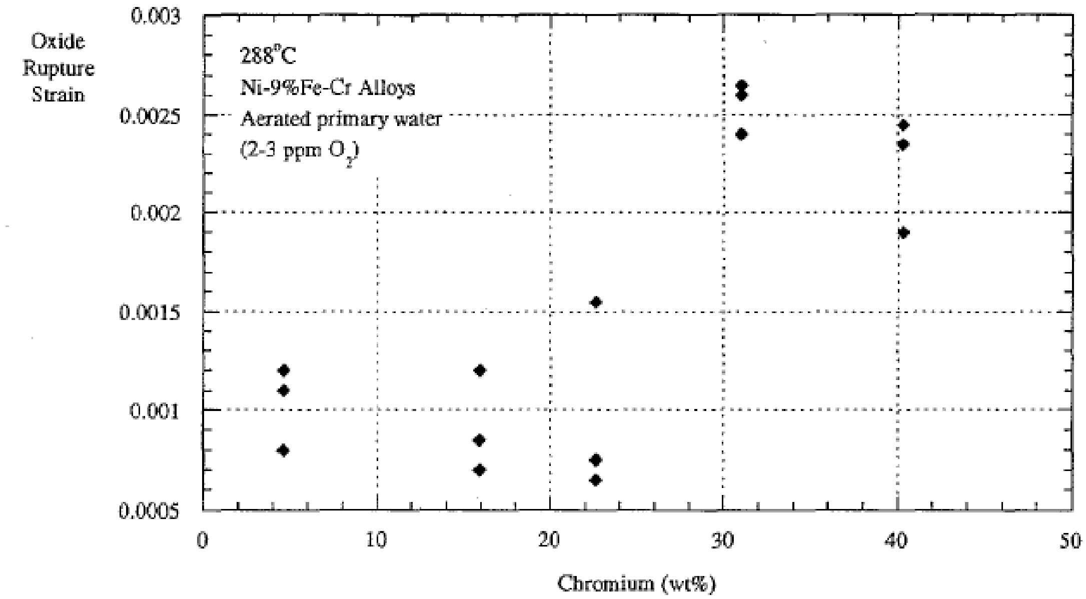


Figure 6. Influence of Cr content on the strain rupture of the film of Ni-9Fe-xCr -alloys tested in the primary water with 2-3 ppm O_2 at 288°C [8].

In Figure 6, one notes that the strain rupture is about 0.0010 in materials with 4.6 to 23% Cr but increases to 0.0020 to 0.0025 for 23 to 41% Cr materials. It is also clear that Cr increases moderately the strain rupture of the oxide (2 to 2.5 times) [8].

3.1.3. Experimental Data about Creep considering the Chromium Effect

It gets here a fundamental issue not only of the discussed model, but also of the SCC process: the understanding of the creep role through the tests carried out by KAPL researchers in Alloys 600 and 690 at 338 °C primary water with 40 cm^3/kg H_2. It were used electrochemically polished uniaxial creep specimens at constant load with the resulting displacement measured with linear variable differential displacement transducers (LVDT) mounted externally to the autoclave (Figure 3). The tests were made above the yield stress, just before the rupture stress (530 to 750 MPa), resulting in actual stresses (instantaneous load/cross-sectional area of specimen). The results are shown in Figure 7: at the bottom left of the graph is noted for both Alloys a primary creep region (0.7 to 1.7 days); from there the test is governed only by the rate of steady secondary creep ($\acute{\varepsilon}_{ss}$): $\acute{\varepsilon}_{ss}$ = 4.7. 10^{-10} s^{-1} for the Alloy 600, about 3 times higher than for the Alloy 690, with $\acute{\varepsilon}_{ss}$ = 1.6. 10^{-10} s^{-1} as expected. Data from this test are consistent with those of Mithieux and Noel and their researchers (1996), according with references [10] and [11] of [8], but Was et al. have shown in 1993 [8] that the values for high-purity Alloy 600 showed creep about 10 times less than the value obtained here (and thus were more resistant to SCC): this fact is attributed to the higher carbon content in commercial alloys.

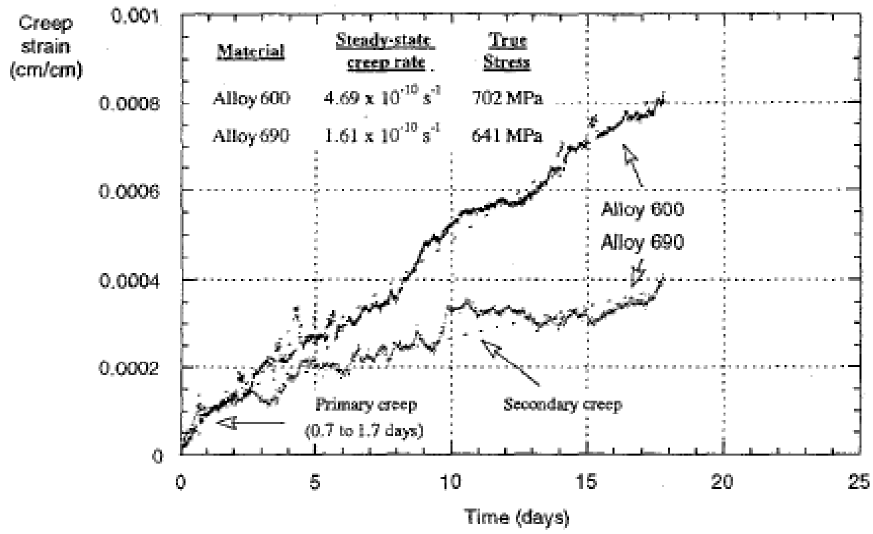


Figure 7. Test result for creep strain vs. time for alloys 600 and 690 in 338°C primary water at indicated stresses [8].

3.1.4. Data Compilation

In Table 1 is summarized the experimental source data on the mechanism of rupture of the passive film of Alloy 600 under conditions of high temperature water: this information is not only important for future improvements of the model, but mainly as a contribution to the formation of a solid data base reference for the PWSCC process of the concerned material-environment condition.

3.1.5. Model´ s Critics

The main limitations of the slip-step dissolution and film rupture model pointed in the KAPL papers are as follows [8], [9]:

a) The secondary creep alone is unable to be the main action factor in the case of the passive film rupture of Alloy 600: there is therefore need for another mechanism to explain the rupture, such as the primary creep;

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Table 1. Experimental data of PWSCC- passive oxide film rupture mechanism of Alloy 600 in high temperature primary water.

Passive oxide film rupture mechanism of Alloy 600-PWSCC	Reference [8]	Reference [9]
Test type	SSRT/CL+anodic polarization tests	CL+ anodic polarization tests
Material/Experimental Environment Condition	Alloys 600/690 at 338 ^{o}C primary water with hydrogen/ oxide rupture test at 288^{o}C	Alloys 600/X-750 at 288 ^{o}C in desaerated primary water
Activation Energy		15 Kcal/mol<Q<54 Kcal/mol
N-Value (or n = -N)	-0.40<N<-0.42	0.5<n<0.7
Passivation Current Density (lower limit)	7.10^{-6} A/cm^2	
Anodic Current Density (higher limit)	i_0= 0.015 A/cm^2	i_0=0.0035 A/cm^2
Time at Repassivation Start	t_0=0.4 s	t_0=0.65 s
Time at 1st rupture	t_r=140 s	550 s (CGR=0.1mil/day) <t_r<26000s (CGR=0.01mil/day)
Rupture Strain	ε_f=0.001	ε_f=0.003
Time to Yield Stress	t_Y=230 s (after this time, it shows sliding slip-steps)	
Crack Tip Strain Rate	10^{-10} s^{-1}< $\dot{\varepsilon}_{ct}$ <10^{-7} s^{-1}	
Total Creep (primary+secondary)		4.2. 10^{-6} s^{-1}< $\dot{\varepsilon}_{ss}$ <1.1.10^{-7} s^{-1}
Steady State Creep (secondary)	1.8. 10^{-10} s^{-1}< $\dot{\varepsilon}_{ss}$ <4.7.10^{-7} s^{-1}	
Total Creep (primary+secondary)		4.2. 10^{-6} s^{-1}< $\dot{\varepsilon}_{ss}$ <1.1.10^{-7} s^{-1}
Primary Creep Effective Time	0.7 days <t <1.7 days	
CGR Range per PWSCC	1.7. 10^{-9} cm. s^{-1}<CGR<1.7.10^{-8} cm. s^{-1}	
CGR Range per PWSCC	8.6. 10^{-10} cm. s^{-1}<CGR<1.1.10^{-9} cm. s^{-1}	Note: Total creep according with eq.(1).

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b) When it considers the primary creep, the crack propagation velocity is slightly lower than those observed.

The stress seems to have a complementary role in the crack propagation velocity, via the multiplicative factor $(K - K_{th})^n$ with K = stress intensity factor; K_{th} = threshold stress intensity factor: for the Alloy 600, $K_{th} = 9$ MPa.√m, according with Scott [4].

The authors of reference [9] endorsed the validity of the model for Alloy 600, but pointed out to incompleteness in the mechanism of cracking by SCC; the reference [8] is very detailed and thorough in experimental data: it pointed to a limitation of this model for stresses below 750MPa, besides confirming the model´ s limitations in fully explaining the SCC failures; also, the secondary creep and total creep deviation are not enough as action factors for the rupture of the passive film. As main result of critical evaluation, more tests should be developed to study rightly the creep influence: this is confirmed also by Hall Jr. [10].

4. A CREEP BASED SIMPLIFIED MODEL FOR SSRT AND CL TESTS

Another interesting issue is that is possible to propose a simplified model based on the reference [8]: in this paper equation (3) is presented.

$$\acute{\varepsilon}_{ss} = C.\ \sigma^{6.64} \tag{3}$$

with: $\acute{\varepsilon}_{ss}$ =secondary creep strain rate; C=constant; σ= stress.

It can be compared with equation (4) from reference [13], adapted for SSRT, since it is possible to establish an empirical relationship between the strain rate imposed in SSRT and the crack tip creep strain rate, which can vary between 1/5 [5] and 1/3 [13].

$$\acute{\varepsilon}_{SSRT} = C_1.\ \sigma^{2.76}.\ t^{-0.5} \tag{4}$$

with: $\acute{\varepsilon}_{SSRT}$ =SSRT strain rate; C_1=constant; σ= stress; t=time.

For CL tests, however it must be used the equation (3) instead of (4), and this relationship becomes even simpler, according to equation (5), leaving the task to validate it.

$$\acute{\varepsilon}_{CL} = C_2.\ \sigma^{6.64} \tag{5}$$

with: $\acute{\varepsilon}_{CL}$=CL strain rate; C_2=constant; σ= stress.

5. A PRELIMINARY COMPARISON WITH BRAZILIAN DATA

Based on Brazilian data average results SSRT with Alloy 600 specimens [14], the crack growth rate was estimated in 5.69×10^{-9} $cm.s^{-1}$ [15], very compatible with [8]. This estimated value has been obtained following that: a) the stress corrosion average crack length was about 100 µm, b) developed in an average time of 488.4 h. This CDTN´ s estimated value was marked over the KAPL ´s results in Fig. 8 (a), showing a very good agreement.

Also, this estimation was according with the estimation based on crack growth rate data extracted from reference [16]: this last paper is very important and influential on PWSCC of Alloy 600 study. In Figure 8 it is showed the comparison between Brazilian data estimated CGR through references [8] and [16].

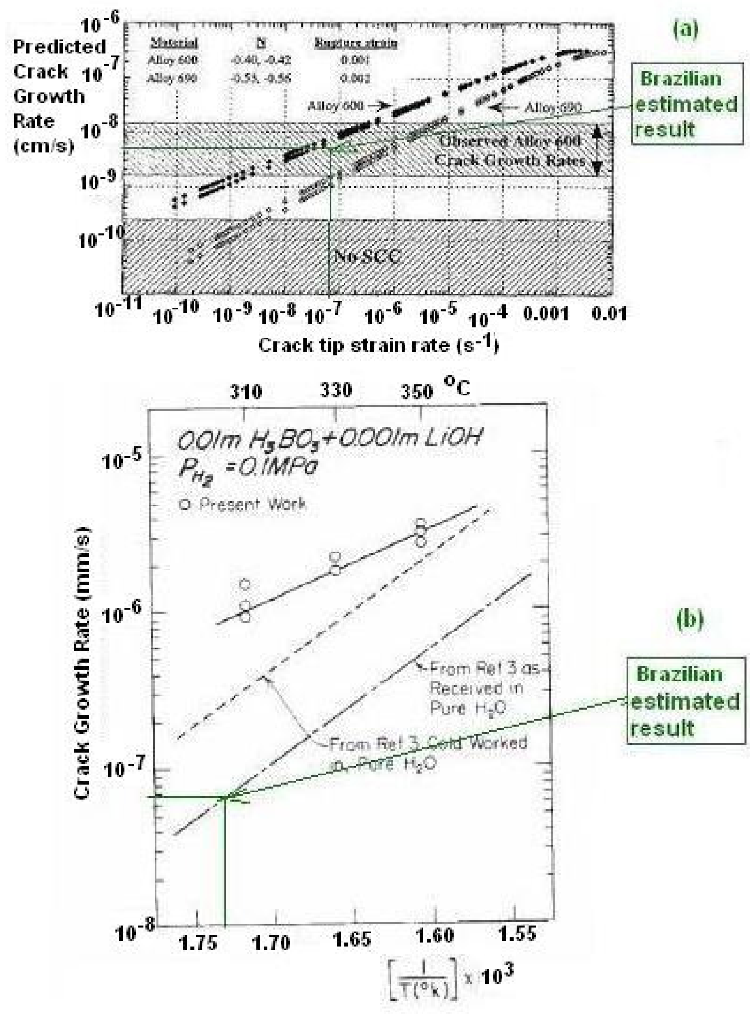

Figure 8. (a) Predicted crack growth rate for Alloy 600 and Alloy 690 at 338°C, based on the film-rupture/oxidation mechanism, as a function of the assumed crack tip strain rate. Marked in green the estimated result obtained by Brazilian CDTN tests. Adapted from [8]; (b) Predicted crack growth rate for Alloy 600 at 303°C, according with reference [16] marked with Brazilian average estimated result.

6. CONCLUSIONS

The aim of this paper was to study the KAPL experiments for the PWSCC modeling data referred to the strain rate crack tip and creep, and their influence in the cracking for Alloy 600. Table 1 was done trying to collect various typical data of the cracking process. Two theoretical simplified models were proposed based in this review, one for SSRT, and another for CL test. Finally a preliminary comparison with Brazilian test data allows a CGR estimation that is according with the KAPL and published literature.

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