
Stress Corrosion Cracking

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1. Introduction

Stress Corrosion Cracking (SCC) is a sudden and difficult-to-predict severe degradation mode of failure of nuclear, petrochemical, and other industries. This chapter aims to give a general view for SCC based in the authors experience on more than ten years working with this kind of failure (mainly in PWR Nuclear Plant) in the Brazilian Energy and Nuclear Research Institute.

SCC is a cause of several serious accidents due to sudden failures difficult to predict, in equipments related to industrial plants, pressure vessels, high pressure piping, ducts, and structures. One gives three following examples: a) Silver Bridge colapse in 1967, over Ohio River at Point Pleasant, West Virginia, USA with 46-killed people [1]; b) Catastrophic disk rupture of a steam turbine from nuclear power plant Hinkley Point Power Station, England in 1969 with enormous material losses, machine destruction, and financial losses due to the long period of operation impeachment [2]; c) Flixborough accident, England in 1974, due to a reactor failure, has caused 28 killed people, several injured people, and big material losses [3].

SCC may be classified as an Environmental Assisted Cracking (EAC), besides Corrosion Fatigue (CF) and Hydrogen Induced Cracking (HIC). The relationship between these three types of failures can be showed in Figure 1 where the EAC domain is the union of the three circles, each one representing the three failure modes. The SCC is caused by three main factors: a) Material susceptibility; b) Environmental condition; c) Tensile stresses (applied and residual). Sometimes CF is considered a particular case of SCC where the load is cyclical, and HIC should be considered as a mechanism of SCC [4].

The EAC scientific interest began in the late 19th century due to apparently spontaneous cracks which occurred in brass cartridges cases belonging to the British Army in India during the monsoon seasons: so they were appealed "season cracks", before when this kind of crack was just understood, and after appealed "stress corrosion crack" [5] – the reference [5] is a comprehensive article which should be read by all that want more information about the historical research of EAC.

SCC normally occurs when one has a material susceptibility, involved tensile stress, and an aggressive environment. In the Table 1, it is showed some common SCC systems [7].

The stress corrosion cracking initiation and propagation is a very complex degradation process, which depends on several parameters; these can be classified in microstructural, mechanical and environmental [8], and its intricate relationship which causes the failure is showed in Fig. (3) [9].

Specific ions and substances which cause damages	Alloys susceptible to SCC	Temperature (°C)
Halogen group		
Fluoride ions	Sensitized austenitic stainless steels	Room
Gas chlorine	Low alloys and high strength steels	Room
Gas iodides	Zirconium alloys	300
Oxygen group (systems H₂O-O₂-H₂)		
Dissolved O ₂ in liquid H ₂ O	Sensitized stainless steels	300
Gas hydrogen in room temperature	Low alloys and high strength steels	Room
Gas hydrogen in high pressure and temperature	Medium and low strength steels	>200
Oxygen group (systems S, Se, Te)		
Politionic Acids (H ₂ S _n O ₆)	Sensitized austenitic stainless steels, sensitized Inconel 600	Room
Sulphydic gas (H ₂ S)	Low alloys and high strength steels	Room
Sulphide impurities in aqueous solution	High strength steels (acelerated hydrogen induced cracking)	Room
Nitrogen Group		
Liquid N ₂ O ₄	High strength titanium alloys	50
N, P, As, Sb, Bi : metal alloy elements	Stainless steels (with Cl ⁻ presence): accelerated cracking	Room
Carbon Group (C, Si, Ge, Sn, Pb)		
Carbonate ions on aqueous solution	Carbon steel	100
CO-CO ₂ -H ₂ O Gases	Carbon steel
Pb ions on aqueous solution	High Ni alloys

Table 1. Specific ions and substances which cause SCC in various alloys, when are present in low concentrations, and as impurities, adapted from [7].

The microstructural factors are [8]: (1) grain boundary chemistry and segregation; (2) thermal treatment which can cause intragranular and intergranular metallic carbide distribution; (3) grain size and cold work or plastic deformation which determine the yield strength: these factors can be described as A in Fig. (3) [9]. The mechanical factors are: (4) applied and residual stresses: these stresses for various geometries can be used as stress intensity K (optionally, strain and strain rate which can be also described related to stresses). 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 Fig. (3); (9) electrode and corrosion potentials E and E₀; (10) partial pressure of hydrogen which reflects on potential.

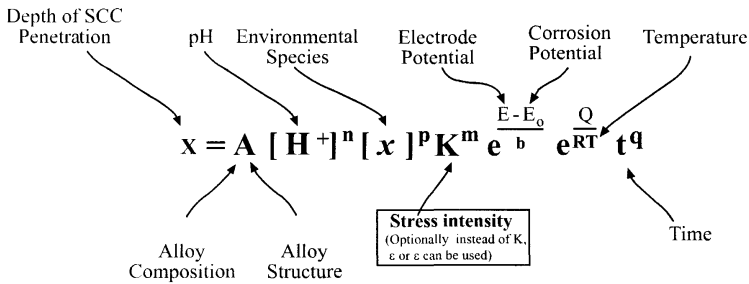


Figure 3. General relationship for SCC process depends on many parameters; where b, m, n, p, q are adjusted constants, Q is the thermal activation energy, and R is the universal gas constant. Adapted from [9].

The time evolution of a SCC could be represented by Fig. (4) [10] where is considered incubation; initiation and coalescence; when K_{ISCC} is reached, a fast increase of the propagation is observed; when the upper bound crack growth rate is reached (Faraday upper bound) an anodic dissolution limit to crack velocity is established, but it may happen more generally be any chemical or diffusion rate limiting process; when K_{IC} is reached the fracture increasing is brittle and produced by mechanical influence rather than environmental influence.

Concerning the parameters described in Fig. (3) which are influent in the SCC, one could note the following: “A” is a parameter which represents the alloy dependence in the SCC process. For example, it will be different to an Alloy whose material grain boundaries present different precipitate patterns: if one considers the nickel Alloy 600 in primary (“pure”) water at high temperatures (upper than 280°C), the SCC susceptibility is greater for a material with few intergranular precipitates than for another material with more intergranular precipitates regularly spaced around the grain boundary contour. Small grains also are less susceptible than greater ones. If the material is cold worked this parameter should be different than a material which did not suffer this treatment: normally cold work material is more susceptible to SCC than the original. So, “A” is a parameter which depends on the thermomechanical treatment imposed to the material: for each heat of material there is a distinct “A”. The pH (“[H]”) and potential (“E” and “E₀”) determine a dominium where the susceptibility to SCC is variable according to several regions (or submodes) of passivity, general corrosion, SCC, and others. Also, according to the electrode potential variation it could occur hydrogen

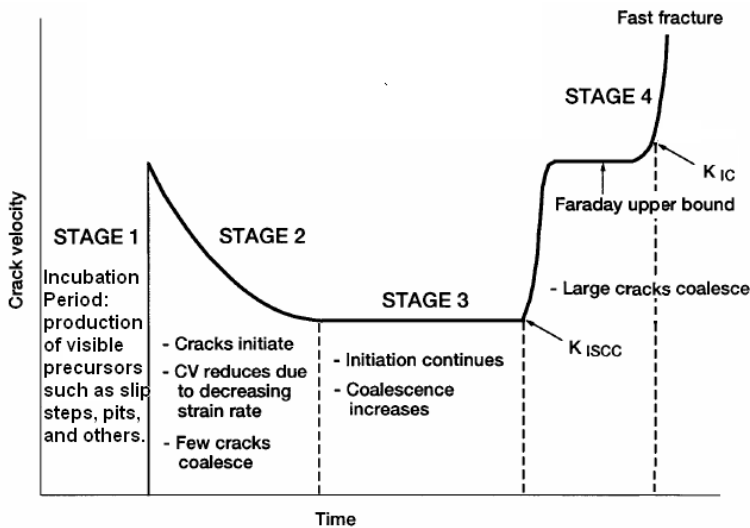


Figure 4. Time evolution of a multiple SCC: adapted from [10].

permeation variation in the material, and this could provoke HIC. Environmental species (“ x ”) are influent on SCC as showed in Table 1. The tensile stress influence through “ K ”-parameter is reflected in the Fig. (4). Temperature (“ T ”) influences the susceptibility to SCC according to the Arrhenius law, then this parameter is showed in the parcel “ $e^{(Q/RT)}$ ”. Finally the time “ t ” is fundamental in the SCC evolution as showed in the Fig. (4) [10].

3. Stress corrosion mechanisms and models

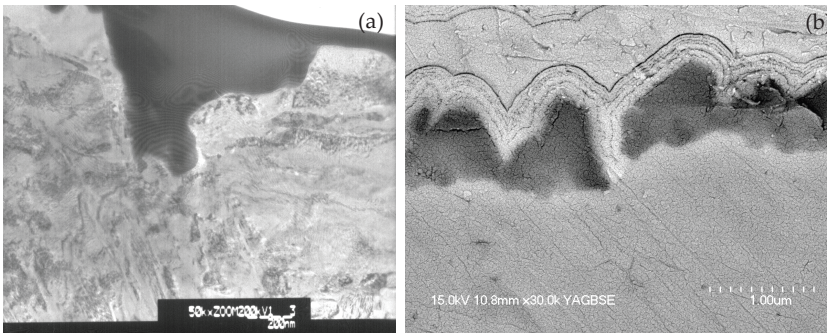
The SCC mechanisms could be classified in two families: Anodic SCC, and Cathodic SCC. The first is governed by anodic metal dissolution and the second governed by hydrogen permeated into the metal which provokes hydrogen embrittlement, and consequently HIC. In the first case are for example, the stainless steels, and in the second the high strength steels [12].

There are several models to represent these phenomena; based on anodic mechanisms: the slip dissolution / film rupture of Ford and Andresen [13], the enhanced surface mobility theory of Galvele [14], the coupled environment fracture model of Macdonald and Urquidi-Macdonald [15]; the internal oxidation mechanism of Scott and Le Calvar [16]; based in cathodic mechanisms: the hydrogen induced cracking models of Shen and Shewmon [17], Magnin and others [18], [19]; based in numeric and empiric observations: the numerical model of Rebak and Smialowska [4], the semi-empirical-probabilistic model of Staehle [9], [20]. For a comprehensive review of several of these models see mainly [8] and [20].

Two important models to be applied in stainless steel and nickel alloys respectively, for nuclear applications are here described, and are anodic: the slip-step dissolution and film rupture

model [13], and the internal oxidation model [16], both applied for SCC propagation. If one substitutes the oxygen action in this last model by hydrogen action, it will be transformed in a cathodic model based on HIC.

The slip-step dissolution and film rupture model is one of the most used engineering models for SCC in nuclear applications, mainly involving stainless steel with boiling water nuclear reactors (BWR) high temperature water: it has been developed in General Electric laboratories [13]. According to the mechanism of this model, crack occurs due to metallic corrosion preferentially along an active path as a grain boundary or crystal slip plane, in an interactive process including electrochemical dissolution and the weakening, rupture and repassivation of the metallic oxide film. The Fig. (5) [21] illustrates partially this process.



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Figure 5. 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. Adapted from [21].

The crack growth rate is postulated to be sustained by periodic strain-induced rupture of the film, and the required rupture strain provided by transient creep. The mathematic expression is given through equation (1) [22].

$$V_{ct} = \frac{M}{z\rho F} \frac{Q_f}{\varepsilon_f} \left(\frac{d\varepsilon}{dt} \right)_{ct} \quad (1)$$

where: V_{ct} is the crack tip growth rate, M is the molecular weight of the material, z is the charge of the anodic dissolved material, ρ is the material density, F is the Faraday constant, Q_f is charge density per film rupture event, ε_f is the oxide fracture strain, and $(d\varepsilon/dt)_{ct}$ is the crack tip strain rate.

Note that the first fraction of the equation (1) is referred to the corrosion anodic dissolution of the material governed by Faraday law. The second and third fractions are referred to the mechanics of the model. Ford and Andresen, from GE laboratories, have simplified this

equation in a form $V_{ct}=AK^n$ where the process is governed by corrosion (Faraday law), tensile stress (through stress intensity factor K), and material interactions with the environment (constants A and n).

An applied example is shown in reference [8] through equation (2), for stress corrosion crack growth in 304 stainless steel and nickel base alloys for BWR, considering strain rate dependence of the stress intensity.

$$V_{sc} = (7.8 \times 10^{-3} n^{3.6})(4.1 \times 10^{-14} K^4)^n \quad (2)$$

where: V_{sc} is the crack growth rate in cm/s, n is an environment and material chemistry parameter related to repassivation rate, and K is the stress intensity in $MPa\sqrt{m}$.

This model has been applied mainly to stainless steel and nickel alloys in light water reactors and other structural materials from nuclear plants, and it's included as a software element in the supervisory systems for component life prediction and evaluation *in situ* of machines.

The internal oxidation model is also used for SCC in nuclear applications, mainly involving nickel alloys with pressurized water nuclear reactors (PWR), and has been developed by P. M. Scott and M. Le Calvar [16]. This model is based on the embrittlement mechanism caused by a layer of adsorbed oxygen atoms which interacts with the material grain boundaries precipitates, and their dislocations. It depends also on oxygen diffusivity on the material. This mechanism could also produce high pressure gas bubbles which enhance the evolution of the intergranular stress corrosion cracking (IGSCC). This mechanism has good agreement to explain SCC in nickel alloys (such Alloys 600 and 690) in high temperature pressurized water of nuclear reactors (PWSCC). The model equation (3) explains the crack growth rate according to this mechanism.

$$V_{IGSCC} = \left(\frac{81kTD_0}{512\gamma^3 a^2} \right) \left(\frac{\delta N_s}{6\pi z} \right)^{1/2} \sigma_p K_I \quad (3)$$

where: V_{IGSCC} is the intergranular stress corrosion crack growth rate, k is the Boltzmann constant, T is the absolute temperature, D_0 is the grain boundary diffusion coefficient for oxygen in considered material, γ is the surface energy, a is the atomic volume, δ is the grain boundary width, N_s is the surface solubility of the oxygen, z is the number of sites explored per gas atom jump, σ_p is the stress contour of the plane strain plastic zone radius of the process crack zone, K_I is the crack tip stress intensity factor.

4. Stress corrosion cracking tests

The applicable types of tests could be classified, according to the stressing modes which are input to the test specimens, in: a) constant total strain; b) constant load; c) constant strain rate

[23] (despite of this report has more than 40 years, it is yet a valuable synthesis of the tests and their comparison). Nowadays it seems that the more usual types of tests are b) and c). This first is normally slower than the second, considered as an accelerated test. This is usually from an order of hundreds of hours, while the other could reach thousands of hours. The specimens could be cylindrical, or prismatic according to the fracture mechanics tests normalization. There are also frequently pre-cracked specimens, rather than plain specimens.

The authors experience is concerned to the slow strain rate test (SSRT), which is a dynamic test where it is imposed to the specimen a slow strain rate through external force over a monitored section, or over a notched region of this specimen, or over a fatigue pre-cracked to the evaluation of SCC material resistance. The imposed slow strain rate is normally between 10^{-4} and 10^{-7} s^{-1} : the local strain rate should be slow enough to make time to occur corrosion processes, and quick enough to cause cracks or damage in a specimen during a reasonable time [24]. The SSRT tests are carried out in accordance with ASTM G 129-95 standard [25]. The specimens are prepared according to ASTM G49-2000 and ASTM E8-2000 standards [26], [27]. The tests are performed at an open circuit potential and the specimens were exposed to the environment for at least 24 hours before applying load to stabilize the surface oxide layer [28]. In the Fig. (6) is showed some exemplified aspects of this type of test [28].

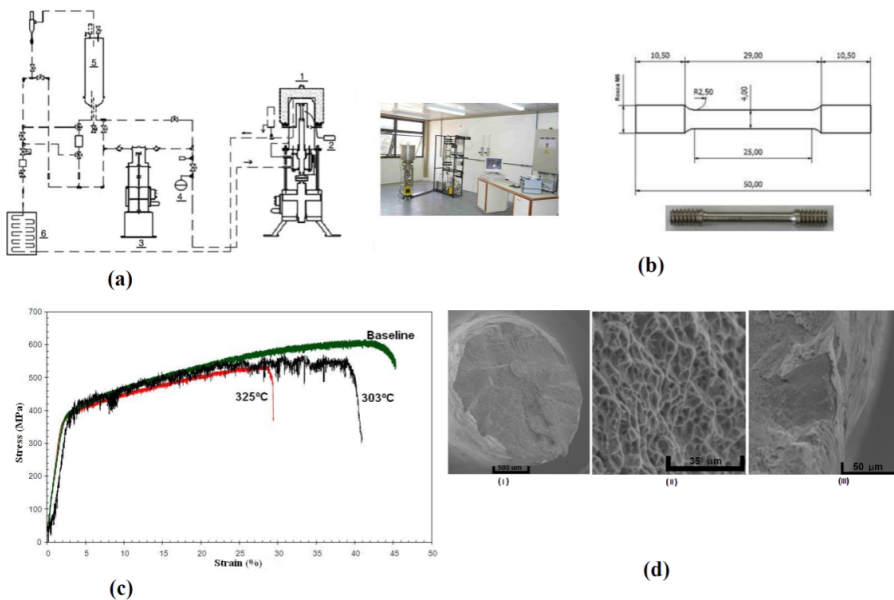
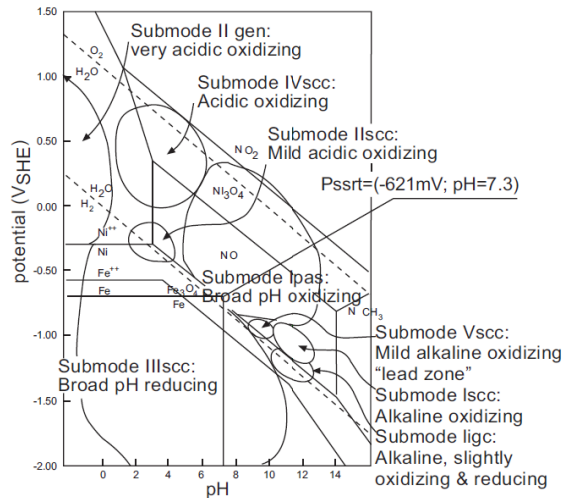


Figure 6. (a) Diagram of the installation for SCC tests: (1) autoclave, (2) Pt electrode, (3) medium circulation pump, (4) pressure accumulator, (5) medium storage tank and (6) cooler, including installation photography: adapted from [24]; (b) cylindrical specimen (mm); (c) Stress - Strain curves of Alloy182 weld of Alloy 182 obtained from SSRT at strain rate of $3 \times 10^{-7} \text{ s}^{-1}$ in PWR primary water condition at 303°C and 325°C; (d) SEM micrographs of Alloy182 weld fractured surface of the SSRT at strain rate of $3 \times 10^{-7} \text{ s}^{-1}$ in PWR primary water at 303°C (a) overview (b) detail of ductile fracture (c) and detail of SCC fracture failure, adapted from [28].

5. Proposed methodology for modeling

The integration between theoretical and experimental parts for SCC modeling is best given to an adequate methodology for modeling. This methodology allows a large overview on stress corrosion cracking phenomenology.

Staele has proposed a three-dimensional diagram [20], which shows the conditions to occur the modes of PWSCC and other corrosion modes on Alloy 600. The base of this diagram is shown in Fig. (7), which represents the potential x pH or Pourbaix diagram for this material in primary water at high temperature (300 to 350°C). One superimposes over it, the corrosion submodes, using experimental data published on literature or from original tests. These submodes are regions of potential where the different modes of surface material-environment interactions can occur, like stress corrosion, pitting, generalized corrosion or passivation. One can put over this 2D-diagram an additional third dimension which represents the “useful strength” of the material as affected by the environment at that point, the strength fraction to SCC. If one replaces the strength fraction to SCC, which is a semi-quantitative measure to SCC susceptibility (and which could be extracted directly from the slow strain rate tests, as a comparative measurement between test in environment of SCC, and in environment neutral to SCC), by kinetic initiation and propagation models to SCC, a generalized methodology to express the SCC can be obtained [20].



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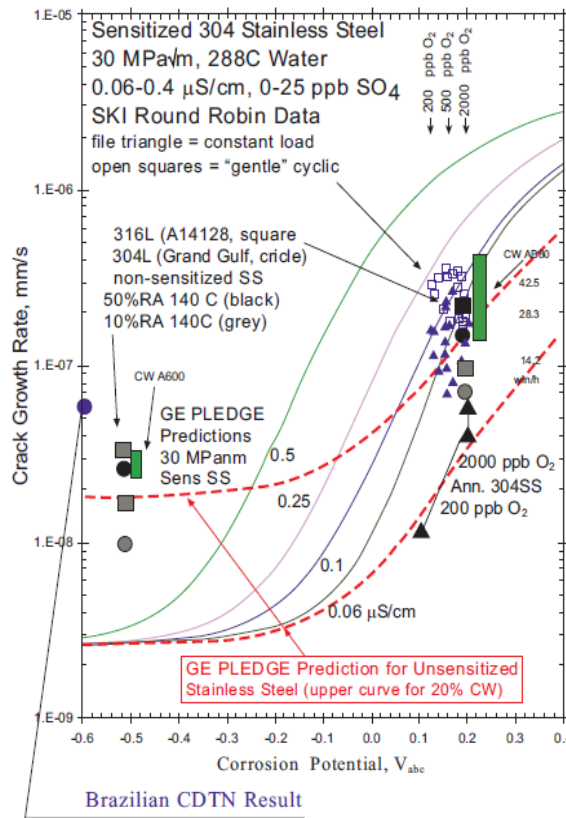
Figure 7. Pourbaix diagram V x pH for Alloy 600 in the range of 300°C used as base marked with submodes regions. The Brazilian CDTN estimated result has been plotted over it (Pssrt). Adapted from [20].

In the D Sc. Thesis [29], a preliminary usage of this methodology was proposed, departing from Fig. (7): first, the SCC susceptibility from tests realized on the slow strain rating test equipment installed at CDTN in Brazil has been marked over this diagram. Literature data

already plotted over the diagram has been proved compatible. After this marked point based on realized tests, it has been supposed different kinetic models. A summary of this work, and some models obtained are in reference [30].

This methodology for modeling could be used, for example, for a Brazilian nuclear power plant, taking into account, the plant materials, and the characteristics of its design and operation, such as the heat material fabrication processes, material composition, plant thermomechanical history, primary water chemical composition, and operational temperature conditions at this plant. Tests can be realized in laboratory (such as CDTN) or from field data.

The methodology is based on empirical-experimental and/or theoretical modeling approaches, such as shown in Fig. (8) which is based in an deterministic similar equation (2) comparison with literature data [31].



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Figure 8. Predicted crack growth rate for Alloy 600 and stainless steel at 288°C, based on the GE PLEDGE Code: it's marked a Brazilian result which was tested at a temperature of 303°C. Adapted from [31].

Then, coupling the obtained modeling curves such as in the Fig. (8) with the point (potential, pH) where the specimen is, over the Pourbaix diagram marked with submodes (Fig. (7)) - this joint information can be used to evaluate the crack growth rate (e.g. according to equations (1) to (3)) of the component which suffers PWSCC at determined submode. If the same specimen is used in another submode (e.g. such as I_{SCC} - alkaline oxidizing or III_{SCC} - broad pH reducing, according to Fig. (7)), the initiation and growth kinetics may be different.

6. Current and future developments

Nowadays there are some tendencies in the SCC studies development: a better understanding of some SCC mechanism factors such as the hydrogen role (hydrogen induced cracks, embrittlement, enhanced plasticity, etc.), and the precipitates (intergranular and intragranular) role in these mechanisms. Another issue is the new test methods for SCC study, such high resolution observations at nanometric scale, through synchrotron, and X-ray tomography. New methods for SCC detection have been developed such as electrochemical noise, acoustic emission. The probability modeling to manage life cycle engineering considering complexes initiation modes such as pitting has been developed. The models have been improved such as the film-induced cleavage. Various of these studies are available in the last Environment-Induced Cracking of Materials (EICM-2) Proceedings [32]. Some interesting works have been developed in important scientific and technological centers such as École de Mines à Paris to a better understanding of SCC [33], and University of Oxford-Department of Materials: in this last, a new experimental approach which enables mechanical testing at micrometric scale, using micromachining cantilevers observed to a focused ion beam (FIB), have been developed. This is applied to study the status of oxidized grain boundaries in the SCC mechanism [34].

It would like adequate to develop various models according to various mechanisms available to different combinations material-environment-tensile tension: it could be done departing of various mechanisms description: an important reference is [35].

Another important issue is the SCC simulation development, which represents a modeling *pari passu* according to a global mechanism performance. Important references of this issue are representing by references [36], and [37].

7. Summary

An overview about stress corrosion cracking approaching according to the authors experience has been given in this chapter. Stress corrosion cracking is a very complex mode of degradation and theme which could be at least adequately developed in an entire book. Authors expect that this overview chapter could be better developed by the research through the essential given references.

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