IMPROVEMENT OF STRESS CORROSION CRACKING (SCC) RESISTANCE BY CYCLIC PRE-STRAINING IN 316L AUSTENITIC STAINLESS STEEL IN BOILING MGCL$_2$ SOLUTION - IMPORTANCE OF THE PRE-DEFORMATION MODE.

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ABSTRACT

Improving the materials resistance to SCC has become a topic of wide interest for theoretical, engineering and financial reasons. The aim of this paper is to propose a process to delay the SCC damage. Recent studies of 316L austenitic stainless steel in boiling MgCl$_2$ solutions show an improvement in SCC resistance by cyclic pre-straining in low cycle fatigue [1]. This improvement consists of an increase in both crack initiation strain and strain to failure, during Slow Strain Rate Tensile (SSRT) tests in aqueous solution.

This paper analyses the effect of pre-fatigue in 316L on its mechanical and electrochemical response to better understand the delay of SCC damage in boiling MgCl$_2$.

The explanation for this beneficial effect is related to a modification of both surface electrochemical reactions kinetics and corrosion/plasticity interactions at the crack tip, due to the particular fatigue dislocation structure.

INTRODUCTION

Resistance to Stress-Corrosion Cracking (SCC) in FCC materials is widely discussed and many models have been proposed in the last ten years. For a review, see [2-3]. Most of them rely to the corrosion-deformation interactions concept.

Recently, a systematic study of the effect of pre-straining conditions on the SCC behaviour of 316L austenitic stainless steels in a boiling MgCl$_2$ solution at 117°C [1] has shown that (i) a tensile pre-straining is deleterious for SCC damage during SSRT tests ; (ii) in contrast, a cyclic pre-straining can delay crack initiation and crack propagation and seems to be a very interesting way to improve SCC resistance.

The aim of this paper is to analyse such improvement in terms of mechanisms through the Corrosion Enhanced Plasticity Model (CEPM) developed some years ago by one of the authors [3]. In particular, the conditions of pre-cycling will be analysed. It will be shown that only pre-cycling to stress saturation improves the SCC resistance of 316L in 117°C MgCl$_2$.

EXPERIMENTAL PROCESS

The material/environment couple tested in this study is the 316L austenitic stainless steel in 117°C MgCl$_2$ solution (30 % weight).

Square samples (4mm width and 12 mm gauge length) were used for SSRT tests, at a constant applied elongation rate of $4.10^{-7}s^{-1}$.

After mechanical polishing, specimens were pre-strained by low cycle fatigue under plastic strain control in tension-compression, at an applied plastic strain amplitude of 10^{-3} for 316L. According to the number of cycles, specimens are then tested in SCC without any further polishing. At an applied plastic amplitude of 10^{-3}, for 316L, the cyclic stress increases, till saturation for N = 50 cycles [3].

The electrochemical potentials are measured with respect to an Ag/AgCl electrode for reasons of temperature resistance. All the collected transients are analysed by electrochemical noise method, including chaos analysis. This method has been shown to be relevant to quantify another kind of localised corrosion, pitting corrosion [4].

RESULTS

Evolution of the Tensile Properties and the Corresponding Electrochemical Potentials.

Figure 1 shows the stress-strain curves for the SSRT SCC tests of the 316L alloy in 117°C in $MgCl_2$ according to the number of cycles during pre-fatigue. Corresponding evolutions of the corrosion potentials during such tests are illustrated on figure 2.
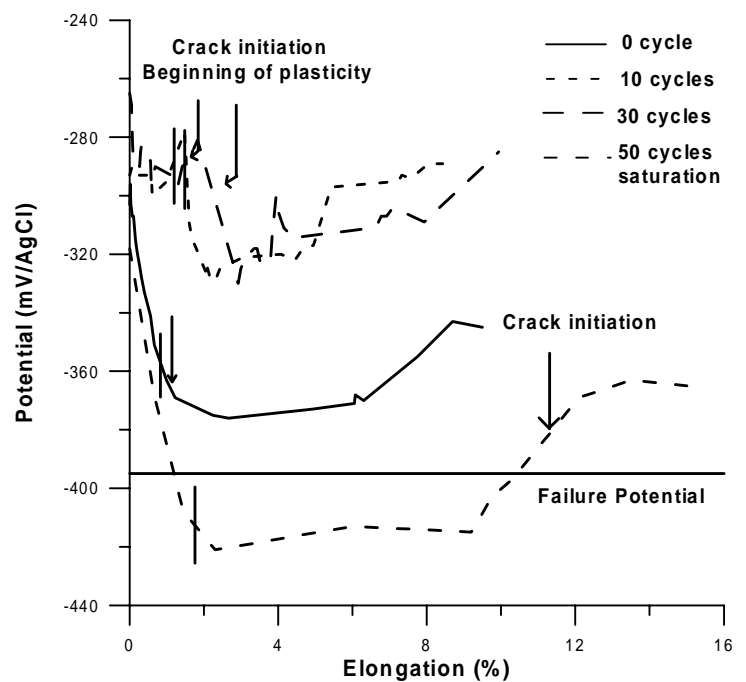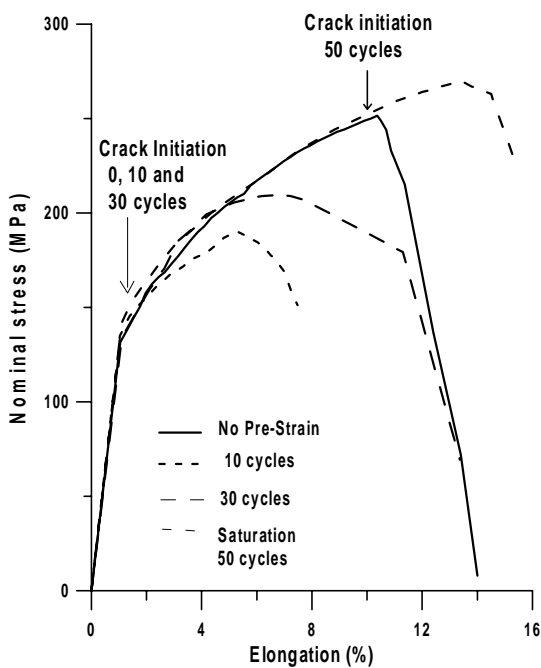

Figure 1 : Stress-strain curves for the various SCC tests - 316 L in boiling 117°C $MgCl_2$ solution.

Figure 2 :Evolutions of the rest potentials. Macroscopic plasticity appears at the elongation marked by vertical bars.

Following observations can be made :
- Only pre-fatigue at saturation (50 cycles at 10^{-3}) has a beneficial effect on SCC behaviour. Crack initiation resistance increases and we shall see in the discussion that crack growth velocity decreases.
- Conversely, cyclic pre-straining can have a deleterious effect on SCC resistance when the number of cycles is less than the one for stress saturation, i.e.,10 and 30 cycles for the applied cyclic plastic strain. Cracks initiate earlier and propagate faster than in the case of no pre-cycling, as we shall discuss later on. Furthermore, pitting corrosion is observed during the elastic deformation of samples pre-cycled before saturation.

- Looking at the evolution of the corrosion potentials during SCC tests, it clearly appears that pre-cycling to saturation allows to decrease the potential below the critical one for SCC initiation [5]. Under this potential, no SCC damage can be observed.
- Samples pre-fatigued before saturation are in fact subjected to strong dissolution effects at potentials higher than the above critical potential.

What we define as crack initiation corresponds to the connection between microscopic observations of the specimen surface and corrosion potentials instabilities (indicated by arrows on figure 1 and 2). Indeed, during the first stages, potentials fall down and stabilise. For specimens pre-cycled before saturation (i.e., 0 10 and 30 cycles) the formation of first visible cracks coincides with the stabilisation of the potential above the critical one. Such a correlation is used to detect crack initiation.

Fatigue at saturation leads to delay the crack initiation time and to decrease the crack growth velocity. A beneficial effect is also found on copper <1 1 0> single crystals in 1M $NaNO_2$ solution at pH 9 [6] and on industrial work-hardened OFHC copper in the same solution.

Fracture Analysis.

SEM analysis in 316L samples after 10 cycles of pre-straining shows that : (i) cleavage-like fracture is generally observed as for non pre-cycled specimens [7], and (ii) a transition from trans to intergranular cracking is observed (figure 3 illustrates such a transition).
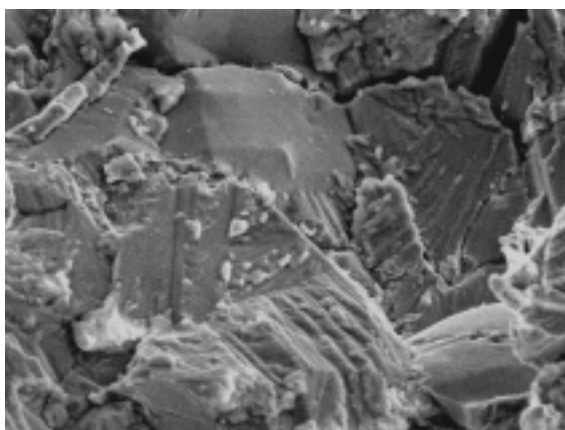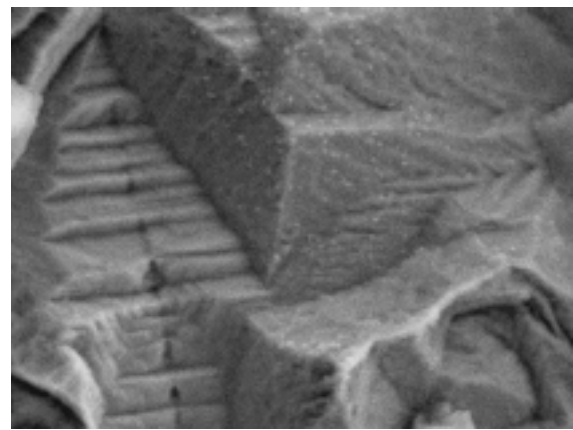
10 microns   *1 micron*

Figure 3 : Micro-cracks and fracture aspects of a 316L sample pre-cycled at 10 cycles. Illustration of a trans-intergranular transition.

Such intergranular cracking is promoted by SCC tests for pre-hardened samples, whatever the pre-hardening conditions [6]. It has been related to higher local stresses at the crack tip and to a faster access to a critical stress intensity factor for a transgranular to intergranular cracking transition.

Effect of the Pre-deformation Mode.

Effect of pre-cycling on the rest potential before and during SCC test

The following curves illustrate the effect of pre-cycling on the corrosion potential before the SCC test (figure 4). This figure shows the values at which the rest potential stabilises before the SCC test according to the number of cycles made.
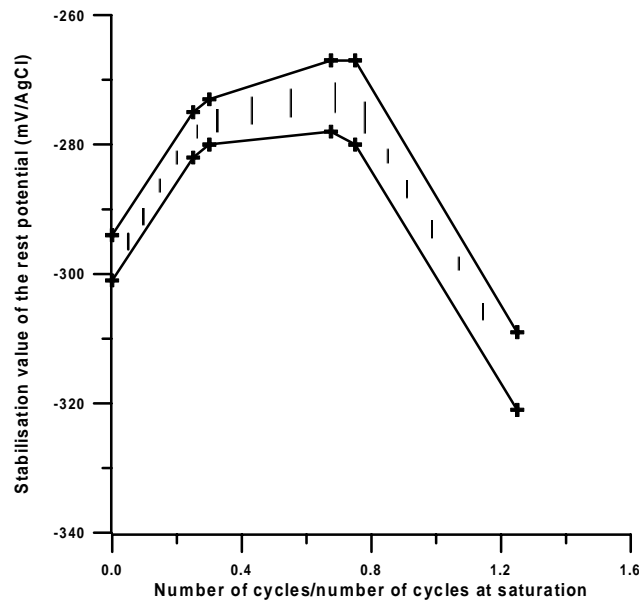
Figure 4 : Zone in which the rest potential stabilises before SCC test, as a function of the number of cycles in pre-fatigue (normalised with respect to the number of cycles to reach the saturation).

The following points can be seen :

- First, the pre-strain induced by the pre-cycling has a quite important effect on the initial stabilisation of the rest potential. If the pre-cycling is made before the saturation, the rest potential is higher than the one obtained for a non pre-fatigued sample. If it is made at saturation, it falls under the potential obtained without pre-cycling.
- The plastic strain during SCC test amplifies the phenomenon observed before the test (beginning of plasticity indicated by vertical bars on Figure 2). Indeed, the potential differences are wider.

In fact, the initial potential is related to the nature and composition of the passive layer formed before the SCC test [5]. It gives information about the way by which passivation occurred. A higher potential indicates a passive layer more sensitive to localised corrosion, while a lower one indicates a possibly more permeable passive layer.

Thus, pre-fatigue has a sensitive effect on the formation of the initial passive layer, i.e. on the dissolution of the sample surface. For specimen pre-fatigued before saturation, it favours a more unstable passive layer, inducing later pitting corrosion during the tensile deformation of the sample. Such an effect is no directly observed on the surface of a specimen pre-fatigued at saturation.

The plastic strain during SCC tests amplifies this phenomenon. Wider potential gaps imply more differences in the dissolution of the samples surfaces, induced by the tensile strain accommodation. Nonetheless, the observed dissolution hardly corresponds to the measured potentials. The more corroded samples are those with the higher potential.

We will discuss in the next paragraph that the occurrence of such potential differences with the unusual observed dissolution clearly indicates some effects of the pre-deformation on the kinetics of the cathodic reactions.

SCC potentiostatic tests.

To further investigate the role of pre-deformation, we realised potentiostatic tests on samples pre-fatigued at saturation. We fixed the potential at –350 mV/AgCl (above the critical potential) as it is a potential related to crack propagation in rest potential tests, for pre-fatigued at saturation and fatigue-free samples (see Figure 2). The stress–strain curves, the current and potential evolutions are shown on the figures 5 and 6.
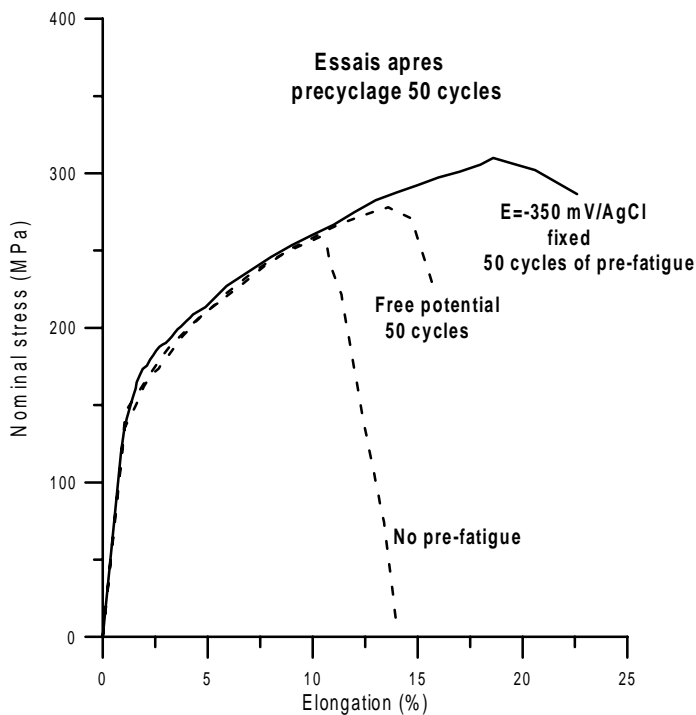
Figure 5 : Stress-strain curves of SCC tests of samples-pre-strained at saturation (potential fixed at –350 mV/AgCl) ; comparison to a pre-strain free sample.
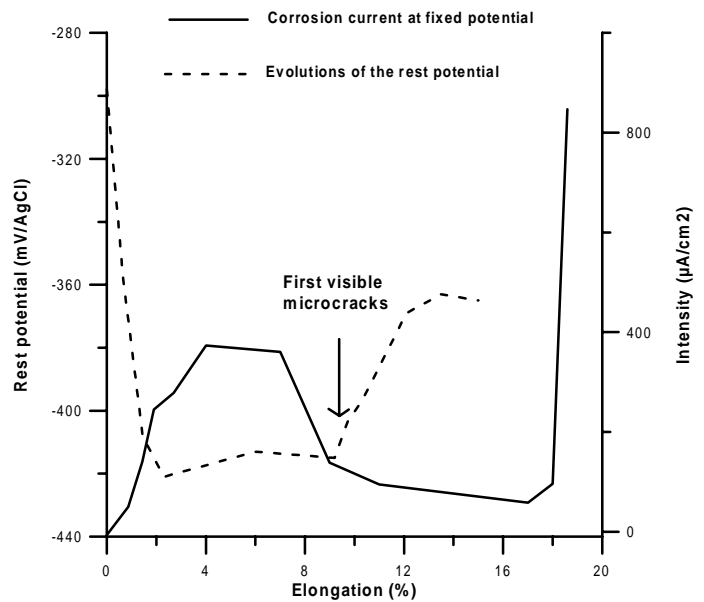
Figure 6 : Comparison of the evolutions of the free rest potential to the corrosion current when the potential is fixed.

Many elements can be noticed :

- Fixing the potential still induces an increase in strain to failure and the first visible cracks still appear around 10 % of elongation, when the potential is fixed. The higher strain to failure (in case of fixed potential, in comparison with the same samples at rest potential) may be explained by the multi-cracking of the samples, in this case.
- At fixed potential, the corrosion current evolves similarly to the rest potential, with a change in intensity level (one decade of intensity) appearing only at about 10 % of elongation. And it has been proved elsewhere [7] that this elongation corresponds to a change in the strain accommodation, as we shall see later.
- For potentiostatic tests, the corrosion current, at the end of the test increases, which is linked to the rapid growth of cracks in the bulk material. Just before this increase, the current appears to have some chaotic characteristics. This topic is under further study.

The plastic strain accommodation is the key parameter for the electrochemical responses of the material.

The beneficial effect of pre-fatigue at saturation is essentially due to the corresponding modification of the electrochemical reactions kinetics on the surface of the sample. This effect is governed by the plastic strain accommodation (discussed later) during the SSRT test, which will further influence the kinetics (levels of potentials) and enable or not localised dissolution and crack initiation.

DISCUSSION

Crack Initiation Delay

The results of figures 1 and 2 show an interesting correlation between the corrosion potentials and the appearance of the first visible cracks. Moreover, rest potentials vary widely according to pre-cycling. Such variations are clearly related to surface fatigue-induced strain, according to the pre-cycling conditions.

Cracks initiate by a strain-induced local breakdown of the passive layer for 316L in 117°C $MgCl_2$ at free potential. This leads to localised dissolution in the slip bands. Thus, the morphology and the repartition of such bands are important parameters to consider.

Pre-fatigue has in fact two interesting characteristics with respect to this point :
(i) It promotes fine parallel slip bands and favours single-glide [3].

(ii) The distance between slip bands decreases with an increasing number of cycles. For 316L, at a plastic strain amplitude per cycle of 10^{-3}, the distance is 15 µm after 10 cycles and about 1 µm after 50 cycles (i.e. at saturation).

During SCC tests, two different aspects must then be considered :
(i) The distance between slip bands is a relevant parameter concerning the reaction kinetics, by means of an anodic/cathodic surface ratio.
(ii) The only stable slip bands are the ones obtained at saturation. This means that specimens pre-cycled at 50 cycles will be able to accommodate the tensile plastic strain with their pre-fatigue slip bands up to 10 % of elongation [7], during SSRT tests, while those pre-fatigued before saturation will not be able to keep their fatigue slip bands. Thus, single glide is longer favoured for specimen pre-fatigued at saturation. SCC crack initiation mainly occurs in slip bands and at slip bands crossing. The crossing occurrence will be delayed for specimens pre-cycled at saturation, not for others.

Saturation is necessary to delay crack initiation, but it is also necessary to have a fine slip distribution promoted by fatigue at saturation. This fine distribution plays a role on the kinetics of the electrochemical reactions. They decrease the dissolution kinetics leading to crack initiation. Two points account for this hypothesis :
(i)   When there are a few slip bands (10 and 30 cycles of pre-fatigue), the rest potential increases (-320 mV instead of –355). Moreover, the corrosion of the samples surfaces is very pronounced.
(ii)   Once the saturation is reached, the slip bands are numerous, parallel and finely located. The dissolution of the surface is poorly pronounced and the potential is lower (-425 mV instead of –355).

Thus, knowing that a lower rest potential corresponds to the production of electrons, one can say that the pre-cycling influences the kinetics of the cathodic reaction. The use of the Evans diagrams (figure 8) shows that pre-cycling before saturation increasing the dissolution rate with a higher potential is possible only if the cathodic reaction kinetics are increased (passage from the lower K curve to the higher one). And, for a pre-cycling at saturation, a lower potential with a lower dissolution rate clearly indicates that the cathodic reaction is "inhibited" (passage from the higher K curve to the lower one).
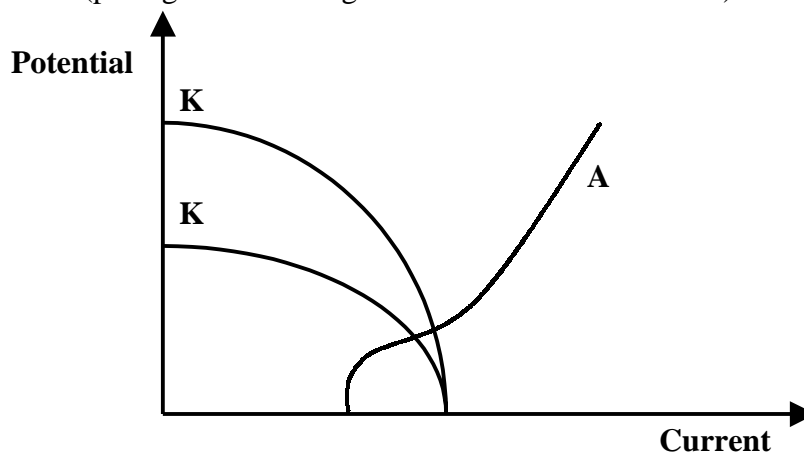

Figure 8 : Schematic Evans diagrams.
K : cathodic curve.
A : anodic curve.

Pre-cycling at saturation is then twice necessary to delay the crack initiation. The first point is that, since the surface strain state induced by the pre-fatigue at saturation inhibits the cathodic reaction, it lowers the rest potential under the critical one and disables the crack initiation. The second point is that the dislocation structure being a low-energy one, it will remain unchanged for a long time during the SSRT SCC test. Consequently, the surface state disabling the crack initiation will remain for a long time and crack initiation will be delayed.

The inhibition of the cathodic reaction might be explained by the adsorbtion of protons on the slip bands. Indeed, at a low potential, no dissolution is observed. This implies that electrons are produced and not used in the cathodic reaction. It may result from a coupling effect between the acceleration of the cathodic reaction (for a low number of cycles) and the very fine location of the slip bands at saturation. These bands being more energetic than unstrained metal, they would make the adsorbtion of protons easier (which would account for the higher potential and dissolution, for 10 and 30 cycles). Then, when the distance between these bands decreases, the adsorbtion of protons would be more difficult and the cathodic reaction is then inhibited. Indeed, if less protons adsorb on the surface, less electrons are consumed. The cathodic reaction kinetics would then be decreased by a slower production of hydrogen (slower consuming of electrons). As a result, this will decrease the dissolution kinetics leading to the crack initiation.

Crack Growth Velocity Decrease.

Pre-fatigue at saturation has also a beneficial effect on crack propagation. This can be understood with the help of the Corrosion Enhanced Plasticity Model (CEPM) [3].
It is based on the fact that dissolution-plasticity interactions at the crack tip generates hydrogen and vacancies which locally enhance the dislocation mobility [8]. Thus two different zones can be observed :
- The very near crack tip zone is softened by the enhanced plasticity in the diffusion distance of hydrogen and vacancies.
- Ahead of this zone, a second one corresponds to the tensile plasticity hardened zone during SSRT tests. A kind of mobile obstacle is formed at the interface between the two zones, corresponding to the diffusion front. Dislocations can pile-up at this obstacle where local k_{1c} [9] can be reached because of stress concentration and hydrogen segregation in the pile-up.

Considering this model, one can understand that the dislocation structure of the bulk play an important role on the resistance of the obstacle to pile-up. If a low energy dislocation structure like in fatigue at saturation is established, the resistance of the obstacle decreases and crack propagation rate decreases too. But if the saturation is not reached during pre-cycling, Lomer locks can form easily which promotes crack propagation because of the formation of strong obstacles.

Looking at Figure 1, one can see that crack propagation occurs at stress levels much higher for pre-fatigued specimen. Calculations of crack propagation conditions were performed elsewhere [9]. They show that the importance of the applied stress on crack velocity is such that the elongation after crack initiation would be much less than that observed on Figure 1 when the applied stress is changed from 150 MPa (non pre-strained samples) to 250 MPa (pre-fatigued samples). Moreover, 250 MPa corresponds to rapid bulk propagation on non-pre-strained specimens.
        According to that effect, one can consider that crack propagation is also decreased by fatigue pre-straining. Such results must be confirmed by SCC tests at applied stress level on CT specimens, with and without pre-straining.

CONCLUSIONS

Through this study we propose a process to delay the SCC damage for a classical environment/material couple, the 316L austenitic stainless steel in a boiling chloride solution. This method consists in pre-straining the material by low cycle fatigue, under plastic strain control, until the saturation of the flow stress.

This beneficial effect is valid for both crack initiation and crack propagation :
First, it induces a homogeneous and fine repartition of strain on the surface, which promotes a modification of the electrochemical reactions kinetics. This leads to a slower dissolution along the slip bands and induces a delay in crack initiation. As long as the dislocation structure of pre-fatigue is not degraded, crack initiation is delayed.
Then it induces a decrease of the crack growth velocity related to the low-energy dislocation structure generated by the pre-fatigue at saturation. These beneficial effects are expected to be more pronounced for SCC tests at imposed stress. This is the subject of further studies.

ACKNOWLEDGMENTS

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