Low cycle corrosion fatigue of zircaloy-4 in iodine environment

Stolarz J., Belouief A., Magnin T., Joseph J.
(1) Ecole des Mines de Saint Etienne, France
(2) Framatome, France

ABSTRACT

A low cycle fatigue study was carried out on semi-recrystallized and on recrystallized Zircaloy-4 under vacuum and in iodised methyl alcohol. Direct observations and monitoring of the electrochemical potential were used to detect different stages of damage. Iodine contained in CH$_3$OH leads to a strong reduction of the fatigue resistance. Surface cracking mode changes from trangranular under vacuum to intergranular in CH$_3$OH + I$_2$. Surface oxidation prior to testing improves the corrosion fatigue life due to a better resistance to crack nucleation.

INTRODUCTION

Power variations in pressurized water reactors cause cyclic stresses and strains in Zircaloy-4 nuclear fuel cladding tubes. Among different U$^{235}$ fission products (rare gases, metals, halogens,...), iodine is generally considered as the most aggressive for Zircaloy-4 in PWR service conditions [1]. Stress corrosion cracking (SCC) of Zircaloy-4 in iodine containing environments has been extensively investigated for many years [2,3,4]. Iodine solutions in methyl alcohol at room temperature are widely used in laboratory studies. Indeed, Cox demonstrated that the SCC behaviour of Zircaloy in gaseous iodine at 350°C was correctly reproduced by tests performed in CH$_3$OH+I$_2$ at 20°C [5]. Many experimental data are available for iodine induced SCC [1], however corrosion fatigue of Zircaloy is much less understood. Studies performed by Schuster and Lemaignan in high cycle fatigue corrosion on Zircaloy-4 plates (recrystallized) and rods (annealed) revealed a strong influence of microstructure and of crystallographic texture on material resistance in CH$_3$OH+I$_2$ [4]. It has been found that crack initiation in corrosion fatigue (CF) occurred through intergranular SCC at high and intermediate stress levels but it was mostly transgranular (as in air) at low stresses [4]. The latter results give an idea about susceptibility of Zircaloy-4 to corrosion-fatigue; however they do not represent correctly the damage conditions in reactor because of a high loading frequency used (10Hz).

In order to better understand the nature of iodine induced corrosion fatigue damage in Zircaloy-4, a low cycle fatigue (LCF) study under plastic strain control in an inert
environment and in iodised methyl alcohol has been undertaken. Reduction of fatigue life is discussed in terms of modifications of microcrack nucleation and propagation modes.

EXPERIMENTAL

Low cycle fatigue and corrosion fatigue tests were carried out on Zircaloy-4 (supplied by FRAGEMA - Lyon, France) containing (in wt %) 1.5%Sn, 0.20%Fe and 0.11%Cr. Smooth fatigue specimens (6 mm diameter) were machined from rods in semi-recrystallized state (pRx) (505°C/1hour). Some samples were subjected to a recrystallization treatment at 700°C during two hours under argon (Rx). Some semi-recrystallized specimens were preoxidized in air before fatigue testing (Ox). Corresponding microstructures are presented in Figure 1.

![Microstructure of Zircaloy-4](image)

The microstructure of the semi-recrystallized Zircaloy is composed of elongated grains with very irregular sizes and shapes. After recrystallization, an equiaxed microstructure is obtained. The mean grain diameter is 20-25μm. A pronounced crystallographic texture is present in both microstructures. The mean orientation of (1 0 -1 1) planes of the hexagonal cell is perpendicular and that of basal (0 0 0 2) planes - parallel to the sample (rod) axis.

Low cycle fatigue tests were performed in symmetrical tension-compression under plastic strain control ($\Delta e_p/2=\pm2\times10^{-3}$ and $\pm6\times10^{-3}$) and at a constant strain rate ($\dot{e}_s/dt=10^{-3}s^{-1}$). In order to avoid any environmental effects on material resistance, vacuum (<10^{-3}Pa) was selected as the reference environment [6]. For corrosion fatigue tests, two environments were used: pure and iodised (0.1 wt% I$_2$) methyl alcohol. Before all corrosion fatigue tests, samples were held in the solution during two hours in order to obtain a constant value of the electrochemical potential (E$_0$). Some corrosion fatigue tests were carried out in pure CH$_3$OH in order to separate the influence of iodine from that of methyl alcohol itself. A sensitive testing equipment is used to record simultaneously the cyclic evolutions of mechanical parameters and of potential transients. In passivating materials like stainless steels or aluminium alloys, electrochemical potential exhibits periodic variations within individual strain cycles which correspond to elementary damage events at the metal surface. Moreover, the evolution of potential peak values versus number of cycles can give precise information about different stages of material damage [7].
The perturbations of the metal-solution interface were characterized using the parameter $\Delta E_T$ which is the difference between the potential values at maximum tensile stress ($E_T$) and at zero stress during load increase ($E_b$). The shape of potential transients within individual strain cycles and the evolution of $\Delta E_T$ versus number of cycles are then correlated with direct observations of surface cracking.

RESULTS

FATIGUE LIFE AND CRACKING MODE

The results of LCF and corrosion fatigue tests are summarized in Table 1.

Table 1. Results of low cycle fatigue tests at $\Delta e_p/2 = \pm 2\times10^{-3}$ (1) and at $\Delta e_p/2 = \pm 6\times10^{-3}$ (2):

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_{\text{max}}$ (1)</th>
<th>$\sigma_{\text{max}}$ (2)</th>
<th>Vacuum (1)</th>
<th>Air (1)</th>
<th>CH$_3$OH (1)</th>
<th>CH$_3$OH+I$_2$ (1)</th>
<th>CH$_3$OH+I$_2$ (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr (pRx)</td>
<td>520 MPa</td>
<td>540 MPa</td>
<td>4000</td>
<td>2900</td>
<td>2700</td>
<td>220</td>
<td>70</td>
</tr>
<tr>
<td>Zr (Ox)</td>
<td>520 MPa</td>
<td>-</td>
<td>4000</td>
<td>-</td>
<td>-</td>
<td>&gt;500</td>
<td>-</td>
</tr>
<tr>
<td>Zr (Rx)</td>
<td>350 MPa</td>
<td>400 MPa</td>
<td>34000</td>
<td>-</td>
<td>-</td>
<td>550</td>
<td>60</td>
</tr>
</tbody>
</table>

In the reference environment (vacuum), fatigue life $N_F$ of recrystallized Zircloy-4 is about ten times higher than that of semi-recrystallized one. This result should be related to the difference of maximal tensile stresses in both microstructures at the given plastic strain amplitude. First surface microcrack nucleation takes place at about 25% $N_F$. The length of such microcracks (type I microcracks according to the classification proposed by Magnin [8]) does not exceed 25 $\mu$m i.e. the mean grain diameter. The nucleation takes place at the intersections of slip lines (bands) with surface (Fig. 2a).

![Transgranular nucleation (32% $N_F$)](image1)

(a) Transgranular nucleation (32% $N_F$)

![Surface crack network at 56% $N_F$](image2)

(b) Surface crack network at 56% $N_F$

Fig. 2. Surface microcracking in semi-recrystallized Zircloy-4 under vacuum ($\Delta e_p/2 = \pm 2\times10^{-3}$)
Between 25% and 95% N_F, a rapid evolution of microcrack densities and lengths takes place (Fig.3) in both microstructures. The surface crack propagation remains mainly transgranular with few intergranular segments. The mean orientation of longer cracks is perpendicular with respect to the sample axis (Fig.2b). At all events, the orientation of crack segments within individual grains remains crystallographic.

![Graphs showing crack density vs. reduced fatigue life](image)

(a) semi-recrystallized

![Graphs showing crack density vs. reduced fatigue life](image)

(b) recrystallized

Fig.3. Evolution of surface microcracking in Zircaloy-4 in low cycle fatigue at Δe_p/2 = ± 2x10^{-3} in the reference environment (vacuum)

In laboratory air and in pure CH_3OH, the fatigue life of semi-recrystallized Zircaloy is reduced by about 30% compared with the reference environment (Table 1). Nevertheless, in these two environments, no qualitative modifications of crack nucleation and propagation modes are observed.

In CH_3OH+I_2, a very strong decrease of fatigue resistance both in semi-recrystallized and in recrystallized Zircaloy takes place. In terms of fatigue life, the best result is obtained with semi-recrystallized and preoxidized (Ox) Zircaloy-4 (Table 2).

Table 2. Reduction of fatigue life N_F(CH_3OH+I_2)/N_F(vacuum) of Zircaloy-4 in iodised methyl alcohol at imposed plastic strain amplitude:

<table>
<thead>
<tr>
<th>Δe_p/2</th>
<th>± 2x10^{-3}</th>
<th>± 6x10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(pRx)</td>
<td>18</td>
<td>57</td>
</tr>
<tr>
<td>Zr(Ox)</td>
<td>&lt;9</td>
<td>-</td>
</tr>
<tr>
<td>Zr(Rx)</td>
<td>62</td>
<td>565</td>
</tr>
</tbody>
</table>

In all cases of corrosion fatigue in CH_3OH+I_2, the surface crack nucleation and propagation become exclusively intergranular, in contrast with LCF in inert environments.

In semi-recrystallized Zircaloy-4 (pRx), at Δe_p/2=± 2x10^{-3}, intergranular cracks are found to nucleate between 10 and 25% N_F (20 to 50 cycles). During the remaining part of fatigue life until the stage of bulk propagation of the fatal crack (N_F=220 cycles), a rapid surface growth of several long cracks (oriented perpendicularly versus sample axis), is observed (Fig.4a). The distance between such cracks on the sample surface is between 0.1 and 1 mm.
In semi-recrystallized and oxidized alloy (Ox), the morphology of longer surface cracks is similar to that observed in the above case. However, at the place of a crack network in, only a single crack propagates on the sample surface.

After recrystallization (Rx), intergranular cracks are nucleated in the very initial stage of loading. After 50 cycles (9% NF), long cracks are present over the whole sample surface (Fig.4b). A rapid propagation of intergranular cracks in the bulk leads to the grain release from the surface (Fig.4c). The surface aspect in the final stage of the test is that of extended intergranular corrosion with areas from which clusters of grains were released leading to a rapid progression of damage in the bulk (Fig.4d).

(a) Zircaloy-4 (pRx) at 68% NF (N=150)  
(b) Zircaloy-4 (Rx) at 9% NF (N=50)

(c) Zircaloy-4 (Rx) at 18% NF (N=100)  
(d) Zircaloy-4 (Rx) at 65% NF (N=350)

Fig.4. Surface damage of Zircaloy-4 in CH₃OH+I₂ at Δf/2 = ± 2x10⁻³

SIMULTANEOUS EVOLUTION OF CORROSION FATIGUE DAMAGE AND OF ELECTROCHEMICAL POTENTIAL

Because of difficulties in direct observations of surface damage during corrosion fatigue tests, the evolution of surface cracking was followed through electrochemical potential monitoring during straining. This method was developed by Magnin [9] in order to study aqueous corrosion fatigue of passivating metals and alloys. The details of its application to corrosion fatigue studies in Zircaloy-4 in iodised methyl alcohol have been presented by Stolarz [10].
The evolution of the potential peak heights is presented in Fig.5. In pure methyl alcohol (Fig.5a), the potential peak increases slightly during first 10 cycles, then it decreases and stabilizes near to N=50. This stage corresponds to the creation of depolarisation sites at the metal surface. In pure CH₃OH, these sites are intersections of slip lines and with surface. A rapid localization of plastic deformation at slip bands leads to a decrease of the area at which depolarisation takes place. It is reflected by a slight decrease of the potential peaks. The potential amplitude remains then stable until N=400, which corresponds to the stage at which first transgranular surface cracks are nucleated (20% Nₚ). Above N=400, a continuous increase of the potential peaks, parallel to the nucleation and growth of surface cracks, is observed. The potential transients recorded within individual cycles exhibit well defined tensile and compression peaks which are characteristic for transgranular damage mode [9].

In iodised methyl alcohol, the potential peaks in annealed Zircaloy evolves in two distinct stages (Fig.5b,c). The initial stage is similar to that observed in pure CH₃OH, with distinct tensile and compression peaks, which correspond to a transgranular surface damage. This stage is much longer in preoxidized Zircaloy: about 200 cycles (Fig.5c) compared with about 20 cycles for annealed Zr4 without preoxidation (Fig.5b). After that, an increase of potential peaks related to the surface cracking is observed in both cases. At this stage, only tensile potential peaks are registered. The absence of compression peaks is characteristic for intergranular damage mode and it is well correlated with direct observations [10]. The stage of surface crack propagation is about 200 cycles both for semi-recrystallized and preoxidized alloy. The surface treatment is thus shown to influence only the nucleation phase of the damage process.

In recrystallized Zircaloy-4, potential transients exhibit exclusively a tensile peak since the first load cycle (Fig.5d). A constant growth of the potential peak takes place from the beginning of the test until final failure. It can be related to the development of intergranular cracking over the whole sample surface. Compared with semi-recrystallized Zircaloy (Fig.5b), the potential peak amplitudes are 2 to 3 times higher. The electrochemical testing method confirms in this way that the very strong reduction of fatigue life in recrystallized Zircaloy (Table 2) is a result of a much higher intensity in electrochemical reactions compared with the semi-recrystallized structure.

CONCLUSION

The presence of iodine in methyl alcohol leads to a sharp decrease of the low cycle fatigue resistance of Zircaloy-4. The surface damage mode changes from transgranular in inert environments to purely intergranular in CH₃OH+I₂. Surface oxidation prior to corrosion fatigue testing strongly improves the corrosion fatigue resistance.

The method of simultaneous monitoring of mechanical and electrochemical parameters during corrosion fatigue tests allows to detect different damage stages. It is shown that intergranular damage in recrystallized Zr4 takes place from the very beginning of the test without any nucleation period as it is observed for semi-recrystallized Zircaloy-4.

The electrochemical method applied confirms fully the results of direct surface observations at different stages of CF tests. The improvement of the fatigue resistance of Zircaloy-4 through surface oxidation is confirmed to result from a better resistance to intergranular crack nucleation, while the crack propagation phase is not affected.
Fig. 5. Evolution of peaks of electrochemical potential transients during corrosion fatigue tests in CH₃OH and in CH₃OH+I₂:
(a) Semi-recrystallized (pRx) - pure CH₃OH;
(b) Semi-recrystallized (pRx) - CH₃OH+I₂;
(c) Oxidized (Ox) - CH₃OH+I₂;
(d) Recrystallized (Rx) - CH₃OH+I₂.
REFERENCES


   Journal of Nuclear Materials, 140, 185-196.

   Journal of Nuclear Materials, 166, 348-356.

   Journal of Nuclear Materials, 166, 357-363.

5. COX, B. 1990. Environmentally induced cracking of zirconium alloys - a review.
   Journal of Nuclear Materials, 170, 1-23.


   Scripta Metallurgica, 19, 1487-1495.


   Proc. ICMS, Beijing.

    Fatigue '96: Proceedings of the Sixth International Fatigue Congress, Pergamon, 667-672.

72