Thermogravimetric experiments coupled with acoustic emission analysis dedicated to high-temperature corrosion studies on metallic alloys

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Abstract

High temperature corrosion of metallic alloys in industrial equipments, such as refinery and petrochemical equipments concerns several phenomena: oxidation, carburization…

These phenomena can create stresses in the materials, the relaxation of which mostly produces transient elastic waves.

Several methods enable the recording and analyzing of these transient elastic waves. Piezoelectric sensors fixed directly on the sample can record elastic waves with a low decrease in energy and frequency at ambient temperature. In case of high temperature environments, a waveguide can also be used to transmit waves from sample to sensors. For this purpose, alumina or platinum are mainly used as waveguide materials because these materials conserve the waveform.

The goal of this study is to assign the elastic waves to the corrosion phenomena. This data base will then be useful for the monitoring of industrial equipment using acoustic emission methods. For this purpose, thermogravimetric analysis (TGA) has been coupled with acoustic emission (AE) devices. Simultaneous measurements of the mass variation and of the acoustic signals emitted during the corrosion of samples of the Zirconium based alloy Zircaloy 4 at high temperatures in the range of 400 °C to 900 °C can provide complementary information to increase the level of understanding of high temperature corrosion mechanisms. Our work focuses on a specific waveguide (WG) conception and on the transmission of elastic waves (acoustic signals) through the waveguide at high temperature. Results on experiments concerning the corrosion of zirconium alloy plates under oxygen atmosphere are presented.

Keywords: Thermogravimetric analysis, Acoustic emission, High temperature corrosion, Waveguide, Elastic waves.

I. Introduction

Iron, nickel, cobalt alloys are broadly used as reactor or container materials in several industrial domains (refinery, petrochemical …). To be able to control the level of damage of these equipments in service represents a major challenge [1]. Corrosion of iron based alloys becomes significant at high temperatures in the range between 400 °C and 900 °C. In order to quantify the level of damage of these alloys, acoustic emission seems to be an interesting method owing to its sensitivity and its non-destructive aspect. AE does neither require ultrasonic signal exciters, nor a heavy infrastructure. The implementation cost of AE systems remains moderate. Acoustic emission measurements can be applicable to equipment in service under various environmental conditions.

This technique has been used to investigate the behavior of different materials at high temperature. Ferrer and al. [2] studied the effect of dimethyl disulfide (DMDS) on the inhibition of the attacks by metal dusting on Incolloy 800 tubes by means of acoustic emission. Acoustic emission experiments were also performed by Schulte and al. [3] to evaluate the sulfidation of ferritic and austenitic steels. Bennett and al. [4] mounted an acoustic emission device into a thermobalance. Works were also carried out by Schmutzler and al. [5] to study the oxidation mechanisms of Fe-Cr-Al by coupling TGA and AE. More recently, Tran and al. [6] also studied the oxidation of titanium, zirconium, nickel and chromium pure metals in a tubular furnace instrumented with an acoustic emission device.

High temperature corrosive phenomena create stresses in the materials; the relaxation of these stresses produces transient elastic waves which can be recorded and analyzed using the AE system. The study of these transient waves enables the anticipation of the degree of damage of these alloys [1]. Several methods are used to record and analyze these transient elastic waves. At ambient temperature, piezoelectric sensors in contact with the sample can record an important number of elastic waves with a low attenuation of the signal energy [7,8]. At high temperature, waveguides are used to transmit the waves from the sample to the sensors; the waveguide design depends on several factors, like wave propagation velocity, wave damping, waveform conservation, experimental atmosphere and temperature. Alumina and platinum are mainly used as waveguide materials [9]; these materials reduce the amplitude and the energy of the signals but they conserve the waveforms [10].

The aim of our study is to associate the elastic waves with the corrosion phenomena in order to be able to monitor the industrial equipment using acoustic emission method. For this purpose thermogravimetric analysis has been coupled with acoustic emission devices to measure acoustic signals emitted during the corrosion of samples at high temperature [11]. Simultaneous measurements of the mass variation and of the acoustic signals can give additional information to increase the level of understanding of high temperature corrosion mechanisms. This work focuses on the good transmission of the acoustic signals via the waveguide at ambient temperature and at high temperature. The selection of the waveguide was applied according to several criteria; one of them is the resistance under corrosive atmosphere. For this purpose, a long waveguide was manufactured in alumina, a material which presents a chemical inertness towards the samples and the different atmospheres. In order to validate the transmission of the waves from the sample to the sensors via the alumina waveguide, two tests were performed. The first test, based on the normalized Hsu-Nielsen method, was carried out at ambient temperature. The second test was executed at high temperature using the oxidation of zirconium alloy plates under oxygen atmosphere at 900 °C to create reproducible elastic waves.

II. Thermogravimetric analysis coupled with acoustic emission

II.1 Thermogravimetric analyzer

Thermogravimetric analysis coupled with the acoustic emission principle was developed in 1977 by R.F. Hochman [12], and then used again by H.J. Grabke [13] and more recently by F. Ropital [14,15]. The experiment consists in positioning a sample on a waveguide inside the TGA furnace and record simultaneously the mass variation and the AE signals using piezoelectric sensors placed in the cold part of the TGA.

In our study, experiments were carried out on a symmetric thermobalance (SETARAM TGA 24) at 900 °C at atmospheric pressure (1 atm) with a gas flow rate of 3 L/h. The TGA equipment is constituted of two symmetric parts; one is used for the sample, whereas the other one is used as a reference. Both parts include a furnace consisting of a graphite resistor which enables to be heated up to 1600 °C. The resistor is surrounded by a dense alumina tube and protected from oxidation by a steady flow of argon. Thermocouples (PtRh 6 % / PtRh 30 %) record the temperature in each furnace. Gases can be analyzed at the TGA outlet using for example the mass spectrometry analyzer, the humidity sensor or the oxygen sensor.

Piezoelectric sensors should be placed as close as possible to the source of the acoustic emission but in the cold part of the TGA on the top of the waveguide. The received signal is pre-amplified and subsequently processed using the acquisition system of the AE (Fig. 1).

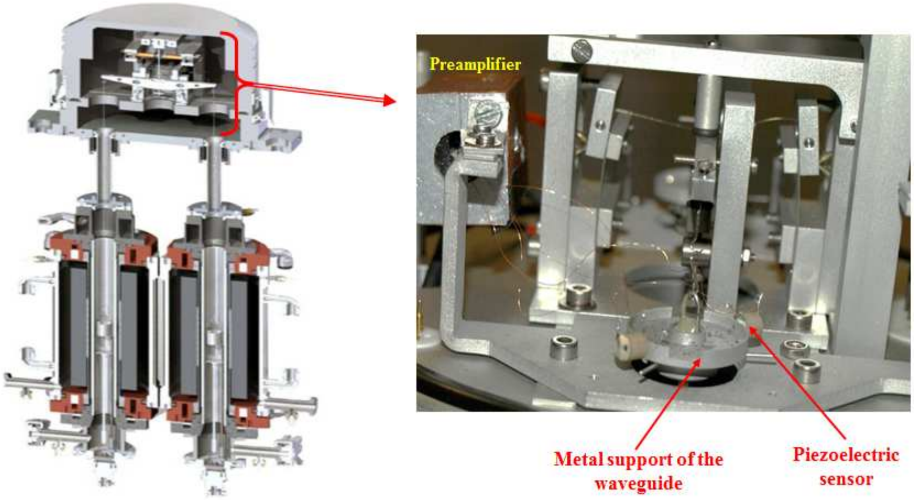


Fig.1. AE acquisition system inside the symmetric thermobalance (TGA 24)

II.2 Acoustic emission

When materials undergo local plastic deformation, cracking or volume transformation, abrupt variations of the field stress take place. This variations lead to elastic energy relaxation. The abrupt release of energy stored in a delimited source region generates high frequency (10 – 1000 kHz) elastic waves called acoustic emission (AE) [16,17]. Crack formation, grain rearrangement, friction between solid surfaces and other grain-scale motions are typical processes which can produce AE. High temperature corrosive phenomena as the growth of oxide layers or the chemical reduction of protective oxides (Al_2O_3, Cr_2O_3) can also produce elastic waves which propagate through the bulk of the material as well as on the surface of the material. Piezoelectric sensors are used to convert these mechanical waves into electric signals.

Discontinuous acoustic emission control (AE event) has been used during our experimental tests. This method is applicable when high energy elastic waves are detected (10^{-11} J to 10^{-4} J). The waveform of the acoustic signals is similar to that one of damped waves. It is necessary to choose adequate AE event parameters (Table 1) in order to analyze the acoustic emission signals. An AE event starts when the signal amplitude exceeds the prescribed threshold (this threshold may be fixed or self-adjusting to the noise level). Further analysis can give more information about the recorded AE signals.

The parameters monitored (counts, amplitude, absolute energy, average frequency…) depend on the objective of each study. For example there may be a close relation between the event amplitude and the level of damage of the material [18,19].

The main parameters used in this study are:

- Event amplitude: the maximum amplitude reach during an AE event (dB_{AE});
- Event duration: the time difference between the first and the last threshold crossing (µs);
- Counts: the number of threshold crossing during an AE event;

- Rise time: the time difference from the first threshold crossing to the event amplitude (µs);
- Absolute energy: integration of the square of the signal deviation from its average: $\mathrm{Eabs(T)} = \int_T |A^2| \, dt\, n$

  Absolute energy unit is attojoule (1 aJ = 10^{-18} J);
- Average frequency: a calculated feature obtained from (Count) divided by (Duration), which determines an average frequency over one AE event (kHz).

In order to record the acoustic signals emitted during the TGA experiments, a specific acoustic device has been developed (transducer, waveguide, acquisition chain). AE sensors were placed inside the cold part of the balance where the temperature does not exceed 150 °C. The sensors are linked to an acquisition chain controlled by the AEwin™ software provided by the Physical Acoustics Corporation Company. Data were analyzed using Noesis™ software provided by the same company. The characteristics of the acquisition chain are given in Table 1.

Table.1. Main characteristics of the AE acquisition chain

Instrumentation	**Sensors**	**Threshold (dB_{AE})**	**System filter (KHz)**	**Model of the amplifier**	**Sampling rate**
Characteristics	PICO 30	25 - 30	10 - 1200	2/4/6 gain : 40 dB_{AE}	0.25 µs (4MHz)

III. Waveguide tests

Our work focuses on a specific wave guide (WG) conception and on its implementation in a TGA device. The waveguide was chosen according to the following criteria: i) chemical resistance against corrosive environments (oxygen or carbon-reductive atmospheres); ii) chemical inertness with regard to the alloy samples; iii) good transmission of the acoustic signals via the waveguide (low attenuation of the signal energy). Following these requirements, a long waveguide was designed in alumina (Fig. 2). Its conception was limited by the internal diameter of the furnace (2 cm) and by the maximal weight that can be supported by the balance (10 g). Samples were placed on a specific support to optimize the contact between the sample and the surface of the waveguide.

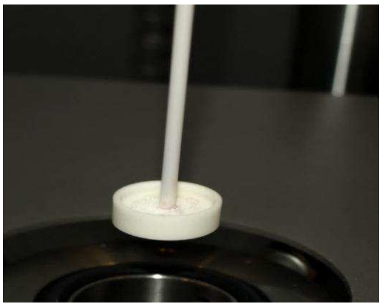


Fig.2. Alumina waveguide

At ambient temperature, the normalized Hsu-Nielsen test (AFNOR NF EN 1330-9) was carried out to verify the AE system. This test simulates an acoustic emission event by breaking a 0.5 mm pencil lead tip against the sample surface. This generates an intense acoustic signal, quite similar to a natural AE source that the sensors detect as a strong burst.

Generally, the lead breaks should generate amplitudes of at least 80 dB_{AE} for a reference voltage of 1 mV and a total system gain of 80 dB_{AE}.

The signals amplitude resulting from our test amounts to 90 dB_{AE}. These results confirm the good transmission of the acoustic signals via the waveguide at ambient temperature.

In order to verify the transmission of elastic waves (acoustic signals) through the waveguide at high temperature, we developed a reference test using the corrosion of zirconium alloy plates (Zy4) under oxygen atmosphere (80 % He + 20 % O_2) at high temperature (900 °C). Oxidation mechanism of this alloy in such conditions is well described [6,20,21]. The oxidation of Zy4 is characterized by an inward oxide layer (ZrO_2) growth on the sample surface. The growth of ZrO_2 layer is associated with a volume increase. The Pilling-Bedworth ratio (R_{PB}) makes a comparison between the oxide molar volume (V_{ZrO_2}) and the corresponding metal molar volume (V_{Zr}).

$$R_{PB} = \frac{V\, ZrO_2}{V\, Zr} = 1.56$$

A R_{PB} value higher than unity means that the oxide layer is exposed to compressive stresses. When these stresses exceed the zirconia fracture resistance ($\sigma > \sigma_f$), cracks occur in the oxide layer and emit AE signals. The record of a significant number of AE signals during this control test may then validate the transmission of acoustic signals through our waveguide at high temperature.

IV. Experimental results and discussion

The experiments were performed on rectangular Zircaloy 4 specimens (4.8 mm x 4.6 mm x 0.5 mm). The chemical composition of this material is presented in Table 2.

Table.2. Chemical analysis of zircaloy 4 samples

Zr	Sn	Fe	Cr	Hf
98.23 %	1.45 %	0.21 %	0.1 %	0.01 %

Thermogravimetric analyses were performed at 900 °C under a mixed gas atmosphere (80 % He + 20 % O_2) introduced by two flow meters with a total gas flow rate of 3 L/h at atmospheric pressure (1 atm). The heating-up (15 K/min) to 900 °C was made under impure helium (traces of water and air). Once the isothermal and isobaric conditions have been attained, the gas mixture (80 % He + 20% O_2) was introduced for 3 hours. The cooling (15 K/min) was done under the same process gas mixture. The AE threshold has been fixed to 30 dB_{AE}.

Blank tests without any specimen were carried out in order to check if the waveguide did not significantly react with the gas mixture. During these tests, the stability of the mass signal validates the chemical inertness of the waveguide. The acoustic signals recorded during the blank tests result from instrumental noise (IN). The characteristics of these AE signals are given in Table 3.

The mass variation of a Zircaloy 4 sample during an oxidation test, mass normalized with regard to the sample surface, as a function of temperature and time is presented in Figure 3. There is a small increase in mass during the heating up which is due to the presence of impurities traces (traces of water and air) in the mixed gas. A significant increase of the mass gain is observed during the plateau under oxygen rich atmosphere with an acceleration of the mass gain rate after 5000 s due to the breakaway which is a kinetic transition. The breakaway corresponds to the cracking of the primary dense thin layer of ZrO_2 leading to a free access for oxygen to the metal oxide interface. After the breakaway the oxidation process is enhanced. The mass gain corresponds to the growth of the oxide layer (ZrO_2) on the sample surface.

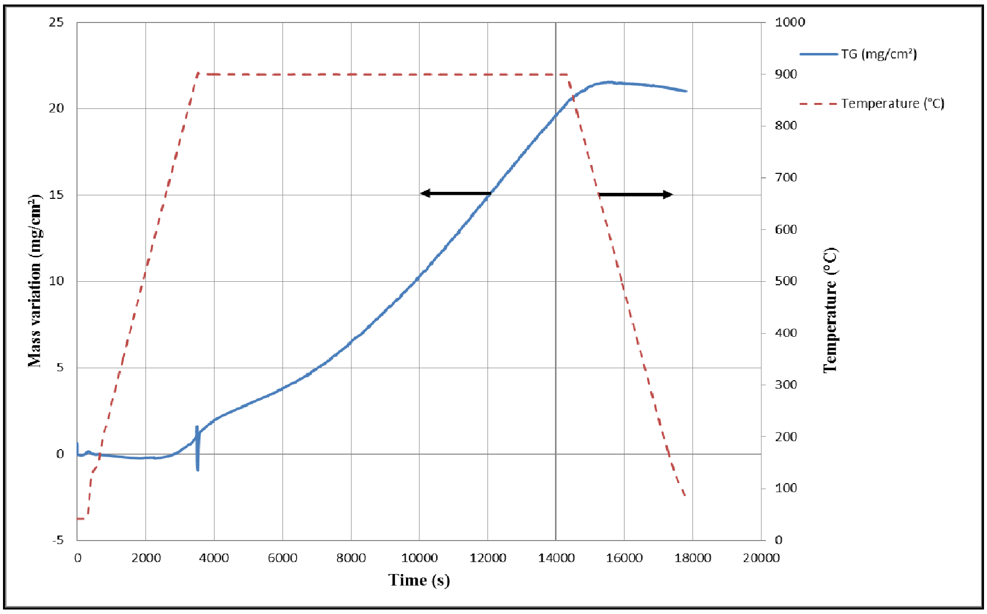


Fig.3. Mass gain variation during Zy4 oxidation test

As predicted in paragraph III, this phenomenon is accompanied by acoustic emission signals. The AE activity, six times higher than the blank test activity at the end of the plateau, increases during the growth of the oxide layer (Fig. 4). According to the graph showing the mass gain rate variation as function of time (Fig. 4), we note that the breakaway occurs after 5000 s. This phenomenon is accompanied by change in the slope of the curve of the cumulative counts (C.C.) during the oxidation test. The wave transmission from the sample to the sensors via the alumina waveguide at high temperatures has been validated by this test.

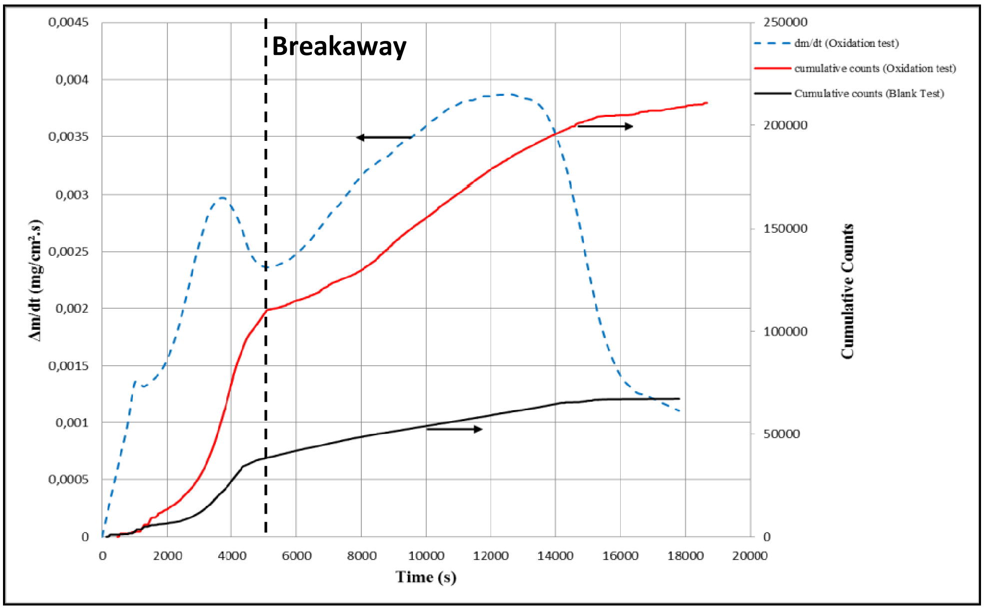


Fig.4. Mass gain rate (mg/cm² s) and cumulative counts variations during the Zy4 oxidation and the blank test, respectively

AE analysis of the data recorded during the oxidation test of Zy4 reveals the presence of three populations of acoustic signals. The parameters of each population are presented in Table 3. Signals assigned to the instrumental noise (IN) are characterized by a very short duration and a low counts' number, 95 % of events of this population are characterized by (1 count – 1 µs). These signals are also recorded throughout the blank test. Events recorded during the isothermal plateau and the cooling are absent during the blank test carried out without any sample. These signals are really linked to the sample oxidation process. Events recorded during the isothermal plateau are characterized by mean amplitudes in the range of (32 – 55) dB_{AE} as can be seen in Figure 5, a high counts' number (tens of counts per event) and a high absolute energy (1 – 2000 aJ). During the cooling, events of very high energy are recorded. They are characterized by a counts' number in the order of magnitude of hundreds of counts per event, a long duration (thousands of µs per event), a high amplitude varying between 55 dB_{AE} and 75 dB_{AE} (as shown in Figure 5), and a very high absolute energy (2×10^5 aJ).The analysis of the average frequency of the acoustics events during the oxidation treatment (Fig. 6) shows that AE signals recorded during isothermal and cooling steps possess a low average frequency varying between 0 kHz and 200 kHz. The corresponding signals assigned to the instrumental noise are characterized by a high average frequency in the range of 200 kHz and 1000 kHz including the resonance frequency of the sensors (300 kHz).

Table.3. The parameters of acoustic signals recorded during the tests

Acoustic Events	Amplitude (dB_{AE})	Absolute Energy (aJ)	Duration (µs)	Counts	Average frequency (kHz)
Instrumental Noise (IN)	**30 - 33**	**0 - 1**	**1 - 4**	**1 - 2**	**300 - 1000**
Isothermal plateau (900 °C)	**32 - 55**	**1 - 2000**	**5 - 2500**	**1 - 350**	**5 - 200**
Cooling (T < 700 °C)	**32 – 75**	**10 - 2×10^5**	**10 - 7000**	**1 - 1000**	**5 - 175**

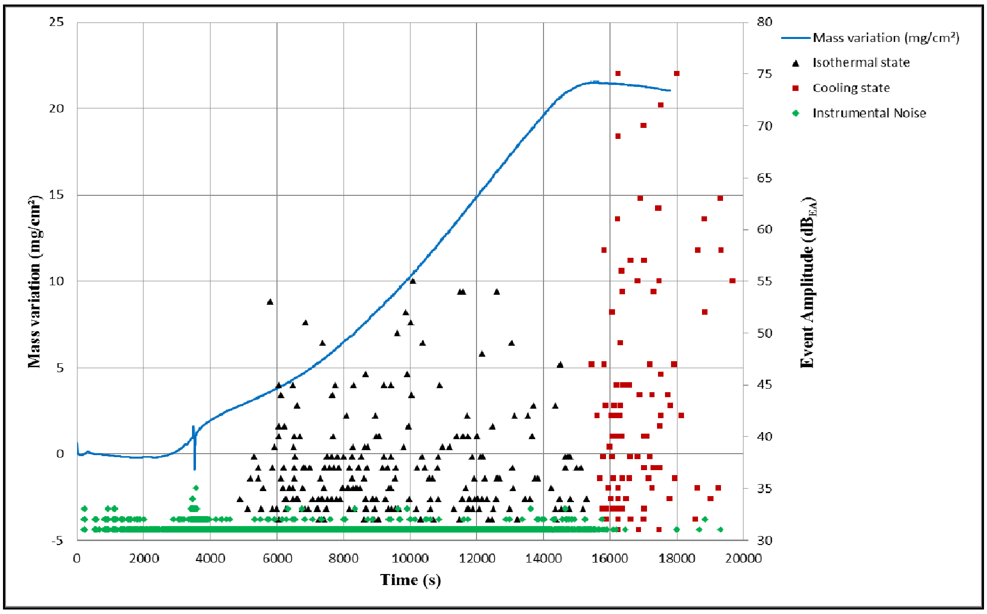


Fig.5. Mass gain and acoustic events amplitudes during the Zy4 oxidation test.
(◆) Instrumental Noise, (▲) Isothermal plateau, (■) Cooling

The knowledge of Zircaloy 4 oxidation mechanism at 900 °C under O_2 rich atmosphere allows us to assign these AE events to the physical phenomena which represent the source of emission of these AE events.

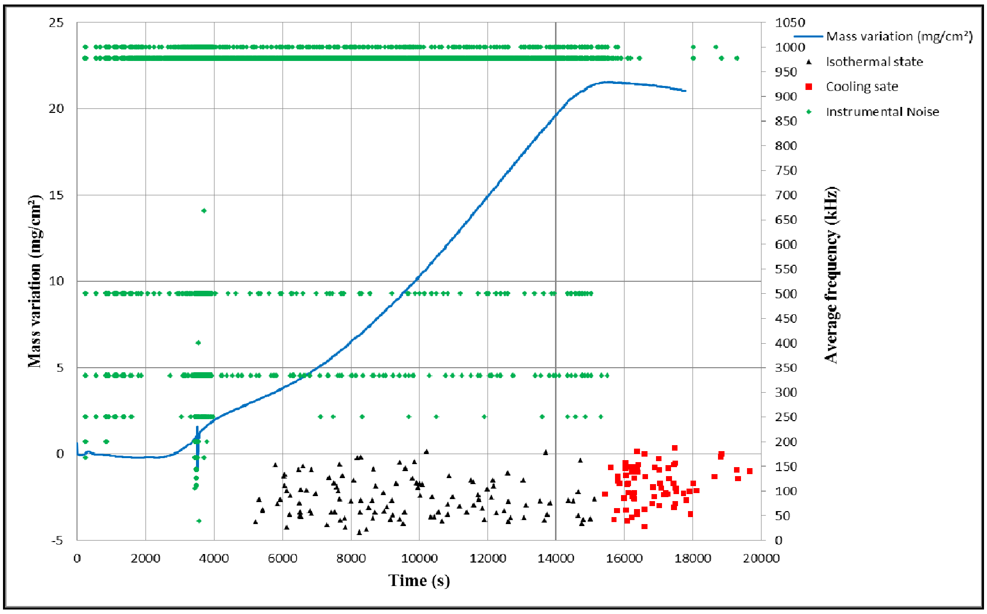


Fig.6. Mass gain and average frequency of acoustic events during the Zy4 oxidation test.
(◆) Instrumental Noise, (▲) Isothermal plateau, (■) Cooling

Cracks have appeared during the isothermal plateau mainly due to the compressive stresses inside the zirconia layer. Furthermore, cracks have appeared during the cooling stage due to the difference in thermal expansion coefficient between the metal and the oxide. SEM pictures of post-mortem oxidized samples (Fig. 7) indicate that cracks are located inside the thick zirconia layer parallel to the metal oxide interface or perpendicular to this interface. The large perpendicular cracks are typically related to the difference in thermal expansion coefficient appearing during the cooling.

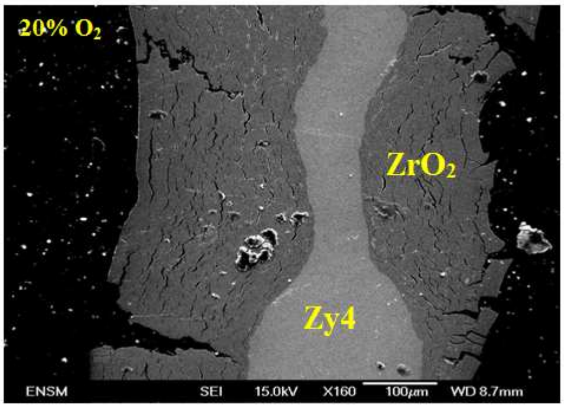
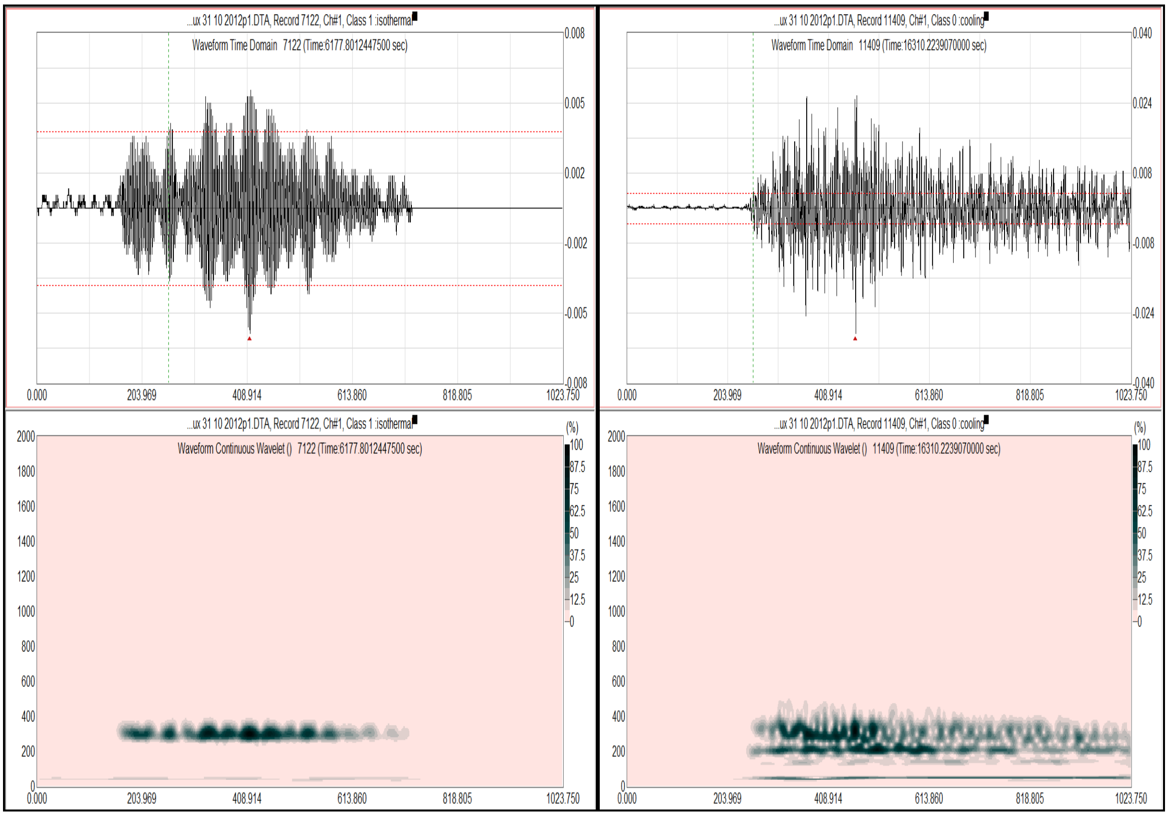


Fig.7. SEM picture of oxidized Zy4 cross section

In order to attribute the acoustic events to the different kinds of cracks (parallel or perpendicular cracks), a detailed AE analysis of the waveform (WF) and of the wavelet transform (WT) was carried out on numerous events in the isothermal part of the treatment and in the cooling part. Figure 8 presents an example of this treatment. The wavelet transform analysis of AE signals recorded during the isothermal plateau (Fig. 8a) possesses an acoustic signature different from the AE signals recorded during the cooling (Fig. 8b). The first wavelet transform is mainly punctual while the second one is more continuous (with some spots).



-a- Isothermal plateau -b- Cooling

Fig.8. Typical AE event recorded during the isothermal plateau (a) and the cooling (b) with corresponding WT and WF.

Combining the wavelet transform analysis as well as the quantitative AE analysis (cumulative count number, amplitude analysis, average frequency analysis) with the SEM observation of post mortem oxidized sample, we can assign the AE events to the different cracks. Oxidation cracks are numerous and they are parallel to the metal oxide interface. The AE signals associated with this phenomenon are numerous and their energy is of medium order of magnitude. Cracks due to cooling are less frequent but characterized by highly energetic events.

V. Conclusion

Thermogravimetric experiments coupled with acoustic emission analysis are an interesting way to improve knowledge on the corrosion of metallic materials at high temperature. In such experimental systems, an important aspect is the transmission of acoustic emission signals from the specimen to the sensors in the elevated temperature range. Furthermore, this waveguide shall not disturb the mass gain measurements.

To ensure a good transmission of signals both at ambient temperature but especially at high temperature, several tests were carried out:

1. A conventional test at room temperature (Hsu-Nielsen test)
2. A specific test at high temperature in the corrosive atmosphere (oxidation of zircaloy 4 under a mixed gas atmosphere of (20 %) O_2 and (80 %) He at 900 °C).

The oxidation of the zirconium alloy induces the growth of a zirconia layer on the material surface. The ZrO_2 layer is subjected to compressive stresses which induce internal cracks. These numerous cracks, parallel to the metal oxide interface, are observed on post-mortem oxidized samples. During the isothermal treatment, the cracks are pointed out by numerous specifics acoustic signals of medium energy. Fewer large transversal cracks are also observed in the oxide layer on post-mortem samples. They are mainly due to the cooling, and the AE signals related to this phenomenon are characterized by a high energy and long durations.

The recording of numerous events during the oxidation test of Zircaloy 4, and furthermore, the correlation of population of signals to different cracking phenomena validated the alumina waveguide design.

Thermogravimetric experiments coupled with acoustic emission analysis using this alumina waveguide will be used to study the metal dusting corrosion of iron based alloys under carbon rich atmosphere.

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