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METHOD COMBINING ACOUSTIC EMISSION AND THERMOGRAVIMETRY FOR AN IMPROVED EVALUATION OF THE HIGH TEMPERATURE CORROSION

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Abstract
To improve the knowledge on the corrosion behaviour of metallic materials, the combination of several physical and chemical methods can lead to major advances. With thermogravimetric methods, corrosion kinetics can be continuously measured without any further information on the physical-chemical processes that occur in the metallic samples. During the last years, some works have been related to the detection of the acoustic emission (AE) signals during wet corrosion processes with good correlation for some localised attacks such as pitting and stress corrosion cracking. For high temperature degradation, acoustic emission can give information on the mechanism of the growth of the scales and on the mechanical stresses that happen.
The coupling of thermogravimetric and acoustic emission techniques appears to be a promising way in order to improve the knowledge on the high temperature corrosion. For this purpose a dedicated experimental device has been developed with special care in order to optimise the transmission of the acoustic emission signals.
This new technique has been applied to study the high temperature gas phase reduction and oxidation phenomena and the formation of catalytic coke deposits under high carbon activity. The behaviour of iron and nickel materials has been compared and correlated with scanning electron microscopy examinations.

1 Introduction

For active degradation processes, acoustic emission (AE) monitoring has allowed some progress for the safety of sensible equipment. AE has mostly been used to control the activity of metallic compounds immersed in electrolytes, where general and localised corrosion generate high energy ultrasonic waves in the materials. Few works have dealt with the control of high temperature degradation by AE. L. Gaillet *et al.* [1] have developed a specific device in order to carry out high temperature degradation under mechanical stress for which AE measurements can be recorded. They found that the sensitivity of the technique was sufficient to study some fundamental mechanisms of the oxidation of nickel. The sulfidation behaviour of segmented tubes made of ferritic and austenitic steels was studied by Schulte *et al.* [2] with AE. They deduced some informations on the behaviour of the scale: the separation (a consequence of the formation and growth of pores) of the outer FeS scale was accompanied with an increase in the AE event rate.
The authors of the present paper have previously demonstrated the feasibility of coupling thermogravimetry and acoustic emission at high temperature. A specific AE transducer of small size has been developed and optimised in order to be incorporated in a thermogravimetric equipment [3]. Preliminary results have been obtained under high temperature carbon attack conditions. The work presented in this paper is more dedicated to the understanding of the mechanisms for the

formation of catalytic coke on iron and nickel samples. The influence of different oxidising conditions of the surfaces of these metals will be discussed.

2 Catalytic coke formation

The formation of carbon filaments which occurs at carbon activities $a_c > 1$ in a range of temperatures 450-700°C is a major problem in many chemical and petrochemical processes where hydrocarbons or other strongly carburizing atmospheres are involved. The carbon deposition on reactor walls induces localised disruption in the process such as heat-transfer reduction and pressure drops. An excessive carbon deposition causes deterioration of the furnace alloys and high cleaning cost.

The formation of catalytic particle on iron is generally explained by the following reaction mechanisms [4-7]:

(1) Decomposition of hydrocarbons at the metal surface (adsorption and dissociation of hydrocarbon molecules) and supersaturation of the metallic phase with dissolved carbon by transfer from the carburizing gas mixture.
(2) When the carbon activity in the metal is higher than the carbon activity for cementite (Fe_3C) formation ($a_c > a_{Fe/Fe3C}$), the supersaturation of carbon in the metal causes nucleation and growth of cementite at the metal surface and at the grain boundaries.
(3) The carbon diffusion is very slow through the cementite in the range of temperature 400-700°C. Consequently, the cementite layer acts as a barrier for further carbon transfer from the gas phase to the metal.
(4) The precipitation of graphite at the cementite surface leads to a carbon activity of $a_c = 1$ at the graphite/cementite interface. Cementite becomes unstable and starts to decompose according to the following reaction: $Fe_3C \rightarrow 3Fe + C$.
(5) Carbon atoms resulting from Fe_3C decomposition are attached to the basal planes of graphite that grow into the cementite. Because of the concentration gradient, iron atoms diffuse through the graphite to the outer surface and agglomerate to small particles (about 20nm diameter). Formation of metal particles is energetically more favourable than complete layers.
(6) These particles act as catalyst for further carbon deposition and growth of graphitic filaments.

The formation of catalytic coke on nickel surfaces does not rely on the formation of a metastable carbide but on the following reaction mechanisms:

(1) Formation of a supersaturated nickel sub-layer with an preferential ingress of the carbon along the grain boundaries.
(2) Graphite germination: beyond a specific concentration of carbon, the solid state super saturated solution decomposes by graphite precipitation that preferentially occurs on defects (grain boundaries, dislocations).
(3) The graphite grow up leads to a grain boundary dislocation and to the formation of catalytic particles.
(4) These particles act as catalyst for further carbon deposition and growth of graphitic filaments.

In this paper, the same conditions of surface treatment (oxidation or reduction) and coking will be compared for iron and nickel samples. Correlations between the coking rate, the acoustic emission noise and the coking reaction mechanisms will be

undertaken with the help of surface observations obtained by scanning electron microscopy (SEM).

3 Experimental device and procedure

The experimental has been fully presented in [3]. Thermogravimetric analyses (TGA) were performed on iron or nickel samples (10 mm x 5 mm x 1 mm) provided by Weber (purity > 99.9%). Before inserting the samples into the furnace, they were first mechanically polished to 1200 grit SiC, cleaned with ethanol and air dried.
In the thermobalance, the samples were suspended with a quartz filament and exposed to a flowing atmosphere at 650°C that has been:
- reductive during 5 hours (60%H_2, 40%Ar) then carburizing (30%H_2, 30% iC_4H_{10}, 40% Ar) (with heating from 20 to 650°C under the reductive atmosphere) or
- oxidising during 30 minutes (60%air, 40%Ar) then carburizing (30%H_2, 30% iC_4H_{10}, 40% Ar) (with heating from 20 to 650°C under the oxidising atmosphere)

The mixture and the flow rate (50 ml/min) were controlled by mass flow meters. All the experiments were performed with a “Setaram TG-DTA 92” apparatus.
In order to monitor AE information, a specific small size AE transducer with a 300 kHz resonance frequency has been developed and optimised for this application [3]. It is stuck on the suspension quarts filament where temperature does not exceed 150°C. Special care has been taken in order to keep a perfect equilibrium of the thermobalance and verify that the additional device did not disturb the mass measurement.

4 Study of the coke deposition on oxidised or reduced iron surfaces

4.1 Study of coke deposition on a oxidised iron surface

The results of the gravimetric and AE measurements versus time are plotted on Figure 1:
- on figure 1a, the mass and temperature variation are recorded versus time,
- on figure 1b, the amplitude of the AE signal is recorded versus time,
- on figure 1C, the cumulated energy and events (hits) of the AE signal are recorded versus time.

TGA plot (1a):
Under the oxidising atmosphere, the 650°C isothermal mass variation follows a standard parabolic oxidation kinetics.
Under the coking atmosphere, two periods of coking are detected: after 500 seconds an increase of the coking rate is measured with an average value of 150 g/m^2h.

AE plot (1b):
During the heating an AE signal is recorded at 550°C: this could be due to the transformation of the magnetite scale (Fe_3O_4) into wustite (FeO). We have observed this phenomena during all the experiments under oxidising heating conditions of iron. During the 30 minutes of isothermal oxidation, the AE activity is very low, that is to say under the 27dB threshold detection of the transducer.
Under the coking atmosphere, an AE signal is detected at the inflexion point of the coking rate. In order to correlate this signal with coking mechanism reactions, specific experiments have been performed in order to analyse by SEM the surface of the iron samples before (Figures 2a and 2b) and after the coking rate inflexion point (Figures 3a and 3b).

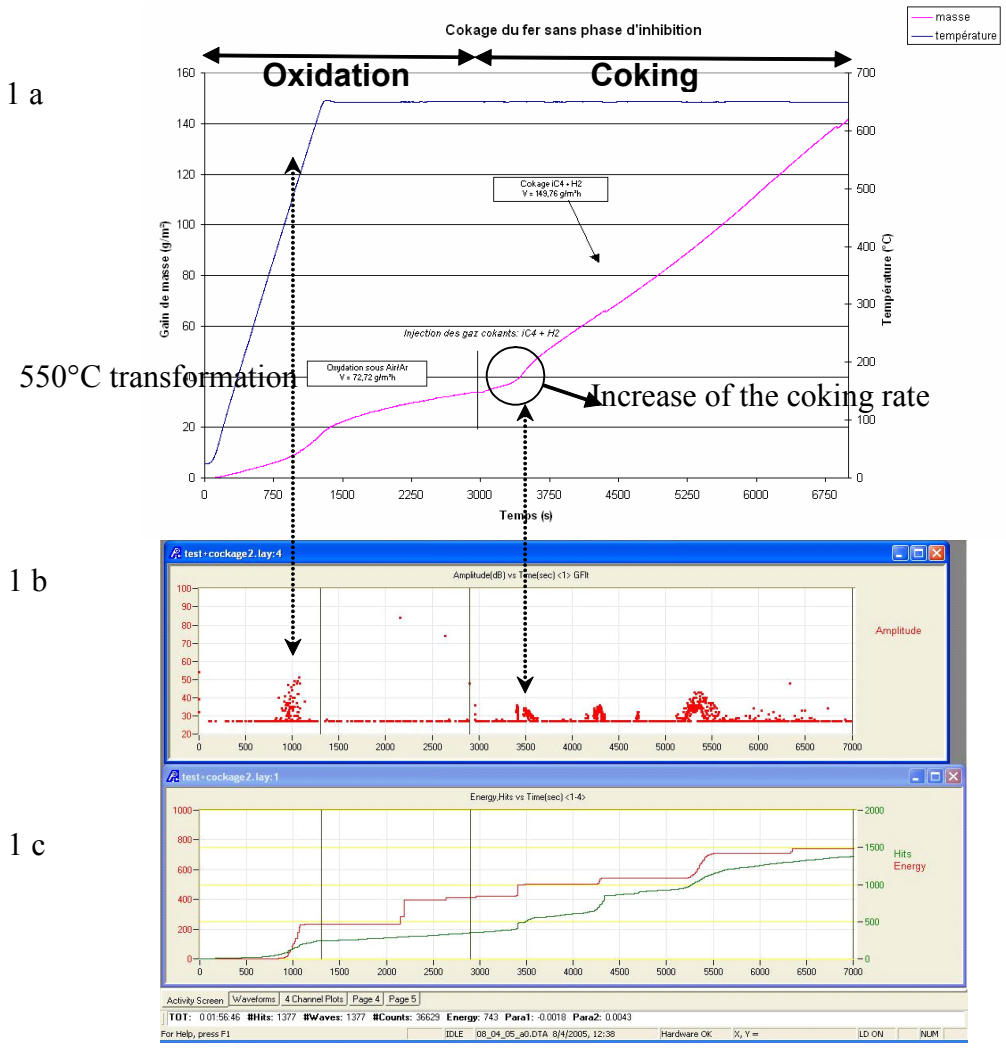


Figure 1: TGA and AE measurements on an oxidised iron surface

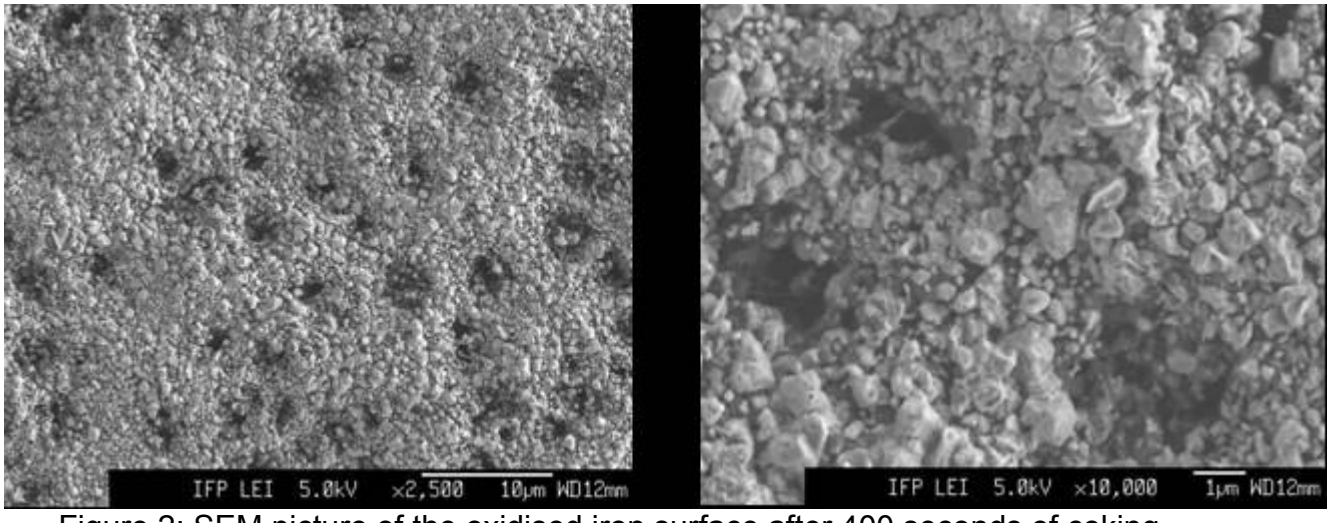


Figure 2: SEM picture of the oxidised iron surface after 400 seconds of coking

After 400 seconds of coking, the oxide layer is porous and carbon has been detected by EDS analysis, in the bottom of the oxide layer cavities (Figure 2).

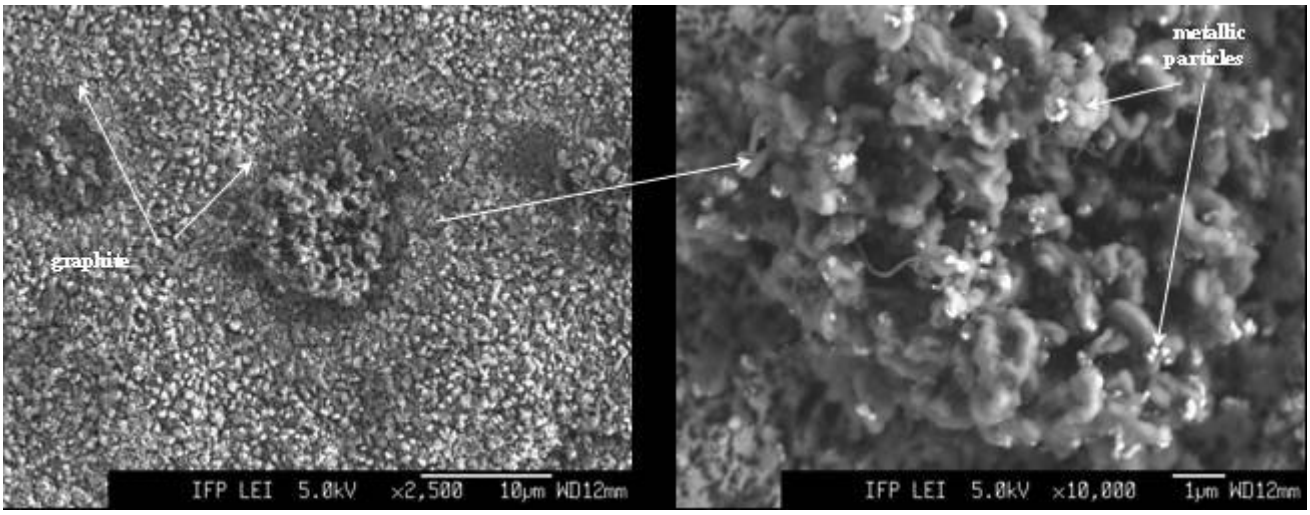


Figure 3: SEM picture of the oxidised iron surface after 700 seconds of coking

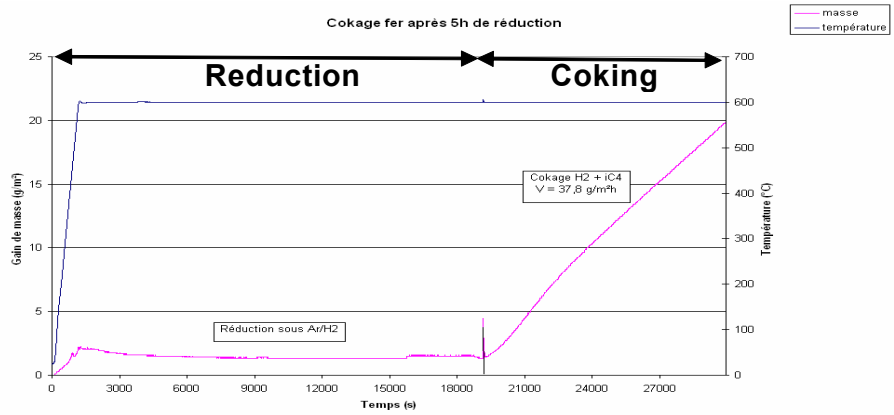
After 700 seconds of coking, many piles of graphite can be observed inside of which the first metallic catalytic particles (cementite) have germinated. These particles start to catalyse the growth of graphitic filaments (Figure 3).

From these experiments, we can suppose that it is the beginning of the formation of the cementite catalytic metallic particles that is responsible of the TGA coking rate inflexion point and of an AE signal.

4.2 Study of coke deposition on a reduced iron surface

The results of the gravimetric and AE measurements versus time are plotted on Figure 4:

4 a



4 b

4 c

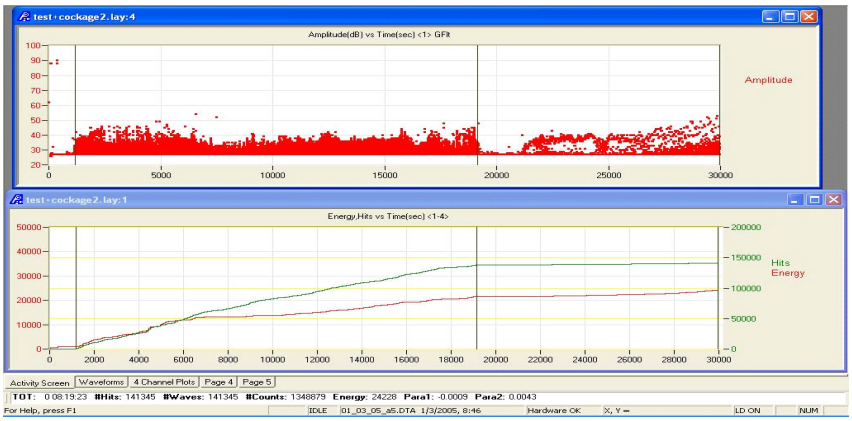


Figure 4: TGA and AE measurements on a reduced iron surface

During the 5 hours of reduction, a small mass decrease is measured in relation with many AE signals.
During the first 2000 seconds, coking does not emit AE signal. Then some AE signals with a moderate amplitude (Figure 4b) are detected but with a small increase of cumulated energy and events (Figure 4c). The average coking rate is 38 g/m^{2}h, which is 4 times lower than the one measured for an oxidized iron surface. These results are in good correlation with some of the authors previous observations [8-9] which indicated that oxidized iron surface are much more active for catalytic coke deposition than reduced iron surfaces.

In order to correlate this signal with the surface mechanism phenomena, specific experiments have been performed in order to analyse by SEM the surface of the iron samples after 5 hours of reduction at 650°C (Figure 5) and after 5 hours of reduction at 650°C and 300 seconds of coking at 650°C (Figure 6).

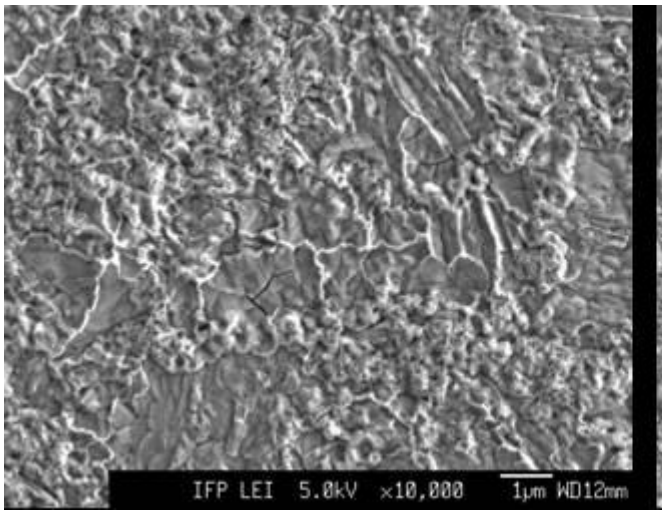


Figure 5: SEM picture of the reduced iron surface after 5 hours of reduction at 650°C

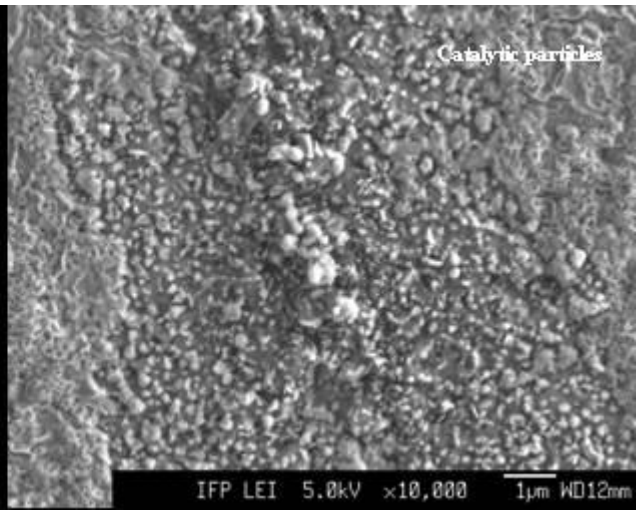


Figure 6: SEM picture of the reduced iron surface after 5 hours of reduction at 650°C and 300 seconds of coking at 650°C

After 5 hours of reduction at 650°C (Figure 5) only a few cracks are observed on the surface layer. Some oxides are still located on the surface and the condition of reduction were not sufficient to fully reduce the iron surface. At the present state of our investigation, we can not conclude on the origin of the AE signal during the reduction period: cracking of the oxide layer, transformation of the oxide to a metallic state, or both of them.

5 Study of the coke deposition on oxidised or reduced nickel surfaces

5.1 Study of coke deposition on an oxidised nickel surface

The results of the gravimetric and AE measurements versus time are plotted on Figure 7.
During the 30 minutes of the oxidation of nickel at 650°C, no significant weigh variation and no AE activity are noticed. When the coking atmosphere is introduced to replace the oxidation one, a single AE signal is measured. Then, even with an important coking rate (150 g/m^{2}h), no AE activity is detected during the 5 hours of coking.

7 a

7 b

7 c

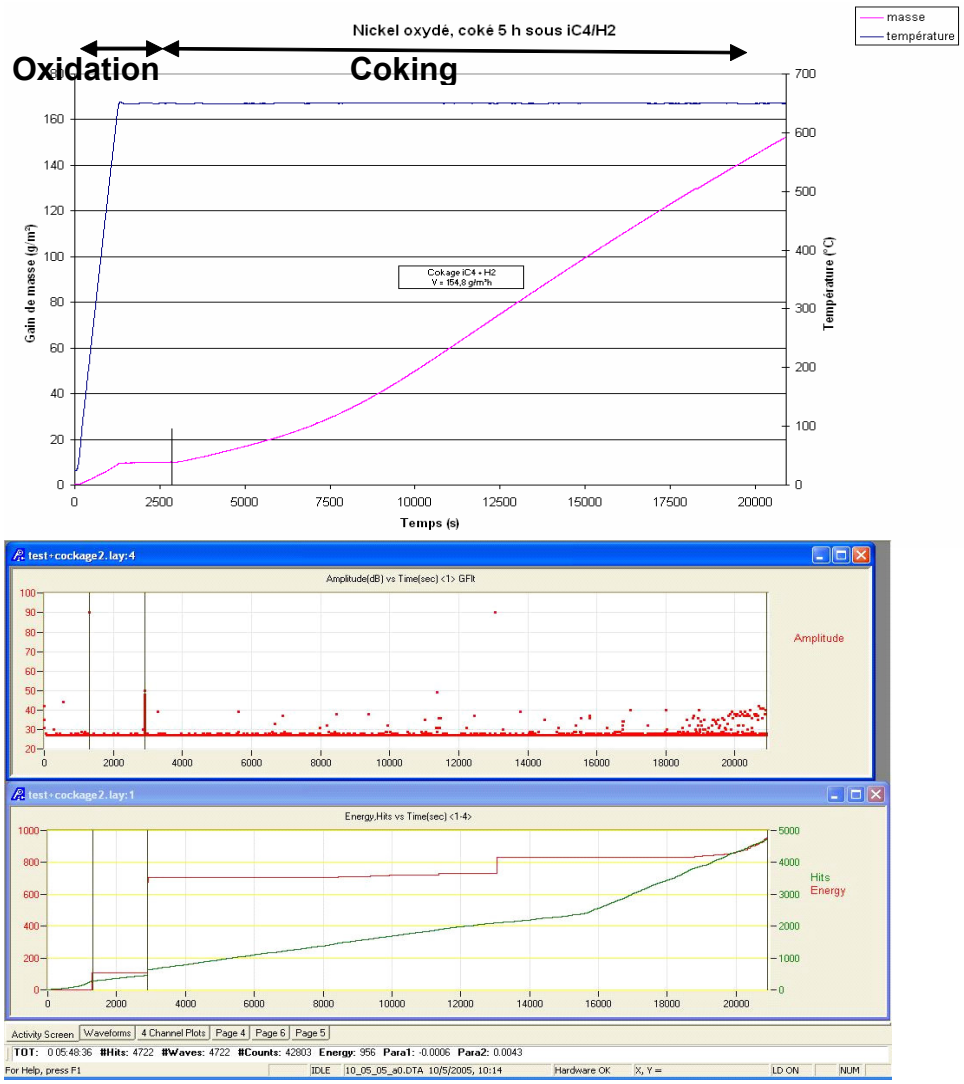


Figure 7: TGA and AE measurements on an oxidised nickel surface

5.2 Study of coke deposition on a reduced nickel surface

The results of the gravimetric and AE measurements versus time are plotted on Figure 8.

TGA plot (Figure 8a):

During the 5 hours of reduction of the nickel sample at 650°C, no significant weight variation of the sample is measured.

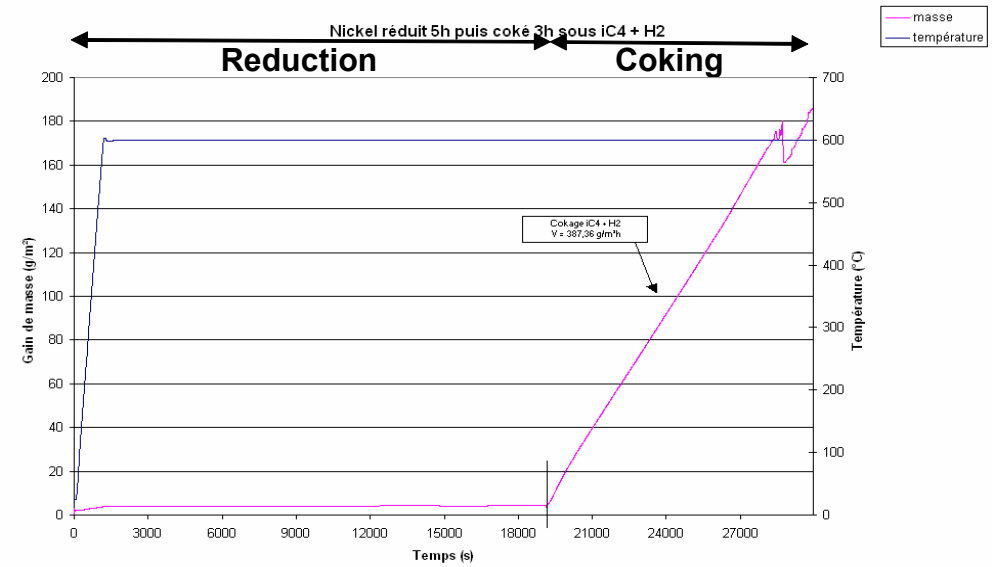
When the coking atmosphere is introduced, a high coking rate of about 400 g/m^{2}h is recorded. Just before the end of the test, some disturbances of the TGA signal are presumably detected due to the fall down of some coke compounds from the sample. Contrary to the iron behaviour, after reduction at 650°C nickel is much more active to form catalytic coke than after oxidation.

AE plot (Figures 8b and 8c):

During the 5 hours of reduction of the nickel sample at 650°C and during the first 2000 seconds of coking, no AE activity is recorded. Then during the next 2000 seconds an important increase of both the amplitude, the number of hits and

the energy of the AE signal is detected. After this period, the amplitude and the number of hits stay constant but the energy of the AE signal decreases.

8 a



8 b

8 c

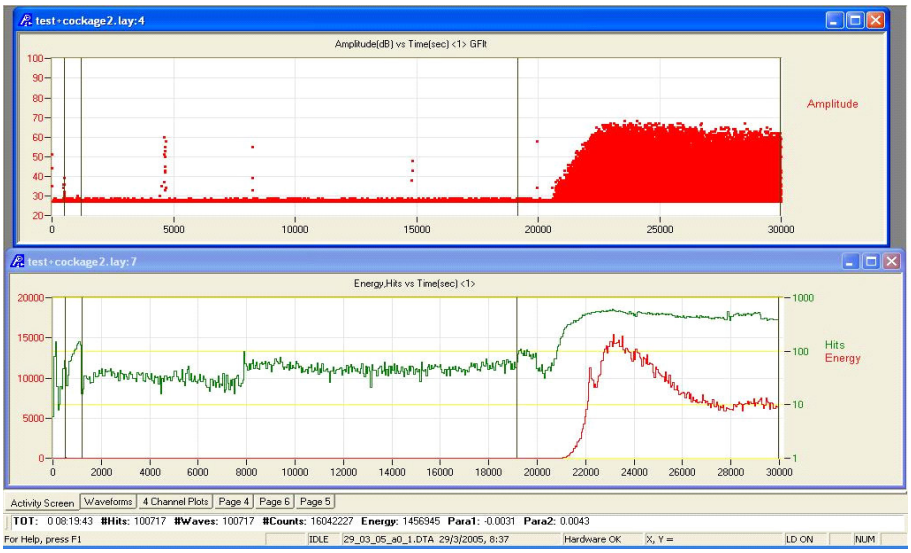


Figure 8: TGA and AE measurements on a reduced nickel surface

6 Conclusion

The coupling of thermogravimetric and acoustic emission techniques appears to be a promising way in order to improve the knowledge on the high temperature corrosion of metallic materials under some of the atmospheres of the refinery and petrochemical industries.

At the stage of our work, the following conclusions can be drawn for pure iron and pure nickel metals.

- the transformation of the magnetite scale (Fe_3O_4) into wustite (FeO) has been detected by the AE methods.
- at 650°C, the reduction of iron is emissive while oxidation does not generate acoustic emission. The origin of the AE could be the cracking of the oxide layer or the transformation of the oxide to a metallic state or both of them.
- at 650°C, both reduction or oxidation reaction of nickel have low AE signal.

- on an iron oxidised surface, the beginning of the germination of the cementite cataltytic particles induces an AE signal.
- on a nickel reduced surface, that is the most active to form coke deposits, the AE activity starts about 30 minutes later after the beginning of the mass increase due to the coke.

These results clearly indicate that, for high temperature degradation, acoustic emission can give information on the mechanism of the growth of the scales and on the mechanical stresses that happen. AE technique can be a promising tool to detect some high temperature damages of metallic materials on site upon industrial structure that will require further R&D work.

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