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High Temperature Behavior of Oxidized Mild Steel in Dry and Wet Atmospheres

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During the hot rolling process, steels develop an oxide scale on their surface. This scale can affect the mechanical properties of the rolled steel and its surface aspect. The main problem comes from the mechanical integrity of the oxide scales which could delaminate or crack, leading eventually to later oxide incrustation within the steel. The objective of the present work is to qualify the mechanical integrity of the iron oxide scales during the hot rolling process. The laboratory experiments use a four point bending test to simulate the mechanical solicitation which takes place during the rolling sequence of the steel slabs. The oxide scales grow on a mild steel at 900°C under wet or dry atmosphere and the oxidized steel is then mecahnically tested at 900°C or 700°C. The high temperature four point bending tests are completed with microstructural observations and with the record of acoustic emission to follow in-situ the mechanical damages of the oxide scales. The results show the role of water vapor which promotes the scale adherence, and the role of the temperature as the oxide are more damaged at 700°C than at 900°C.

Keywords *: four point bending test-acoustic emission-oxide scale adherence*

1. Introduction

The steel sheet making is generally performed by the hot rolling process which allows to transform the steel slabs into coils. The slab is a gross product of solidification obtained at the end of the continuous caster. Before entering the first rolling stand, the slab is re-heated at about 1200°C. During this stage, an oxide layer is formed at the surface of the slab; this scale is called the primary oxide scale. The thick primary oxide scale (thickness is approximately between 500 and 1000 µm) is removed with pressurized water which acts thermally and mechanically.[1)] The slab then enters a serie of roughing mill stands. During roughing mill, the slab is again oxidized at the surface and some oxide scale (secondary scale) is formed. This secondary scale is partially removed at the end of the roughing mill in order to obtain a good surface state. Actually, a bad surface state would be a major source of surface defects during the end of the rolling process (finishing mill). Then, when the slab enters the finishing mill, the scale thickness should be small (generally less than 10 µm). At the entry in the finishing mill, the steel is at about 1000°C. Its thickness is about 30-40 mm and is reduced to a few millimeters after the last rolling stand. At the end of the finishing mill, the steel sheet is coiled for storage. During coiling, the temperature of the still is around 600°C. Tertiary oxide scale is formed during the finishing mill and descaling apparatus are generally used to remove this scale between two rolling stands. The presence of the tertiary oxide scale during the finishing mill can generate many defects at the surface of the metal sheet and at the surface of the work roll.[2)] One of these defects is particularly due to scale residues which subsiste after the descaling operation. These residues can be embedded in the steel during later passage under the rolls. Other defects come from the scale spalling and the scale cracking during the hot rolling process. Then it is important to consider the parameters which determine the adherence of the oxide scales and more generally the mechanical damages that could occur in these scales.

Actually many parameters should be considered to well understand the adherence and the mechanical behavior of the oxide scales. In the present study, we will limit these parameters to the nature of the surrounding atmosphere,

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taking into account the presence of water vapor which might help for the adherence of such oxide scales, in some cases. Another important point is the temperature variation which induces a large evolution both of the corrosion resistance and of the mechanical properties of the scales because of the very distinct ductile/brittle temperature transition of each of the three oxide phases present in the scales.

In order to conduct such studies, a special apparatus has been developed; it consists in a high temperature chamber with controlled atmosphere. Metallic samples are introduced in a four point bending test set-up and placed in the high temperature chamber. The four point bending loading is used as it well reproduces the mechanical influence of the rolling sequence.

2. Materials and experiments

The four point bending tests at high temperature and under controlled atmosphere are performed in a special set-up developped in our laboratory. This set-up is sketched in Fig. 1. The high temperature chamber allows to heat the sample up to 1000°C. The use of a secondary pumping system allows to reduce the pressure down to 10^{-7} mbar in the chamber. The atmosphere is controlled thanks to a gas entry equipped with a microvalve. The usual gas used in this set-up are nitrogen, oxygen or synthetic air. Another entry allows to enter a mixture N_2+H_2O which is produced by passing nitrogen through water maintained at a given temperature. In the present study, this temperature is fixed at 60°C to obtain a relative humidity in the high temperature chamber equals to 21%. A third entry is connected to an $^{18}O_2$ tank which is a container of zeolite used to trap oxygen at very low temperature. To release oxygen 18 and inject it in the high temperature chamber, the tank is heated. To pump down oxygen 18 from the chamber and recover it, the zeolite tank is cooled down with liquid nitrogen.

From a mechanical point of view, the metallic sample is placed within special alumina holders to perform the four point bending tests. These holders are placed at the end of an alumina cane which is introduced in the high temperature chamber. Load and displacement are recorded during all the experiment, and in situ analysis (in temperature and under atmosphere) of the sample damage is performed using acoustic emission during all the experiment. The acoustic emission sensors are placed outside the high temperature chamber and the alumina cane is used as a waveguide between the sample and the acoustic sensors.

The samples are prepared from rolled plates of a low alloyed steel which chemical composition is given in Table 1. They are 1 mm thick and the surface dimensions are 20x5 mm^2. For each sample, one face is covered by a chromia layer (1 µm thick) which protect this face to later oxidation.

The metallic face which will be subject to corrosion

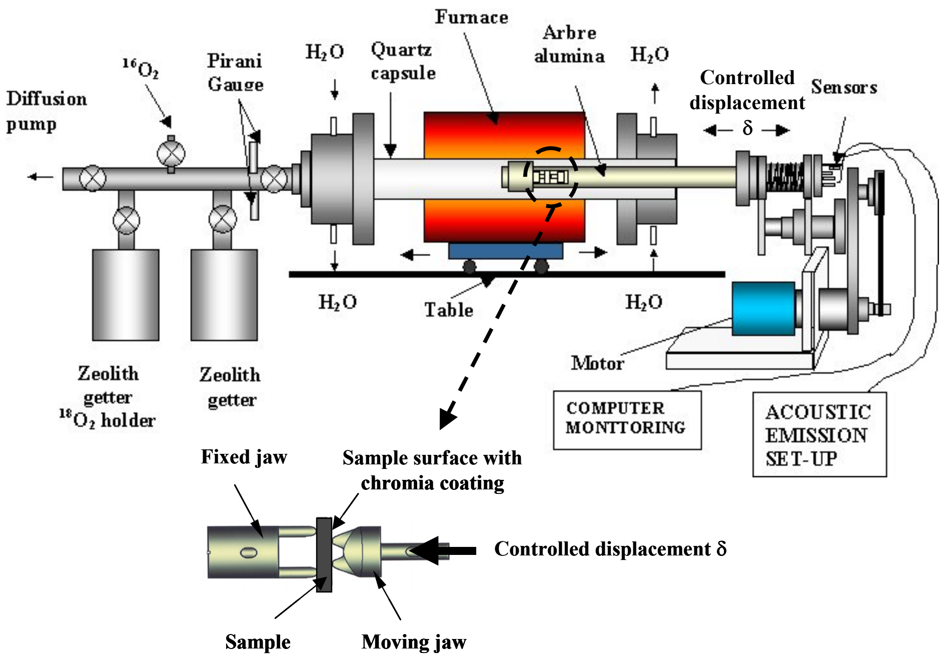


Fig. 1. Shematic drawing of the high temperature four point bending test under controlled atmosphere

Table 1. Chemical composition of the steel used in the present study

Chemical species	Fe	C	Mn	Al	Ni	S
Weight %	Bal.	0.82	0.85	0.75	0.5	0.33

is first polished with abrasive paper (SiC) until grade 1200. It is then cleaned and dried. In the four point bending holders, the sample is placed in such a way that the chromia layer is under compression during the test (Fig. 2).

The test procedures has been developped in order to represent conditions which are closed to the rolling conditions. Then, the sample is placed between the alumina holders and is heated up to 900°C under dry nitrogen at the normal pressure. After the temperature stabilization, the sample is annealed at 900°C during 9 minutes under the wet mixture N_2+H_2O. Then the wet atmosphere is replaced by dry nitrogen and the temperature is fixed at a given value T which is 700°C or 900°C. Such a temperature variation represents the thermal effect which takes place when the steel is in contact with the work-rolls. After thermal stabilization, the four point bending test is performed. Finally the sample is slowly cooled down to room temperature.

During the four point bending test, the force, F applied on the sample and the displacement, δ of the moving jaw are recorded as a function of time. From these recorded data, calculations are performed to obtain the maximum stress value at the top surface of the sample, σ, and the sag, s. For this purpose, the following equations are used:

$$\sigma = \frac{M_b}{I} y \quad (1)$$

where M_b is the maximum bending moment between the two jaws.
I is the moment of inertia
y is the distance to the neutral fibre

The maximum bending moment, M_b is calculated as follows:

$$M_b = \frac{F}{2}\frac{L}{2} \quad (2)$$

The moment of inertia is obtained by:

$$I = \frac{bh^3}{12} \quad (3)$$

The dimensions of the sample, L, b and h used in equations (2) and (3) are defined on Fig. 2.
The sag, s is defined by :

$$s = R\left(1 - \cos\frac{a}{2R}\right) \quad (4)$$

with:

$$R = \frac{1}{2}\sqrt{\frac{\left(a \cdot l - a^2\right)^2}{4\delta^2} + a^2} + \frac{h}{2} \quad (5)$$

The parameters a and l are defined on Fig. 2.

During the four point bending test, the acoustic emission signal coming from the sample is recorded. Two kind of emission are recorded:

- A continuous acoustic emission with a weak energy (10^{-13} to 10^{-10} J); This type of signal is often associated with the movement of dislocations,[3] and is observed mainly during the plastic deformation of metals.
- A discontinuous emission with a higher energy (10^{-11} to 10^{-4} J), which is related to microscopic or macroscopic damages like crack propagation, corrosion,⋯

For the present study, the discontinuous acoustic emission is the most interesting. To record the acoustic signal, a threshold value is first defined. This value is the limit beyond which the acoustic salve is recorded. Such a salve is a damped oscillatory wave (Fig. 3) which is defined by the following main characteristics:

- Amplitude: the maximal peak amplitude
- Rise time: the time between the first overshoot of the

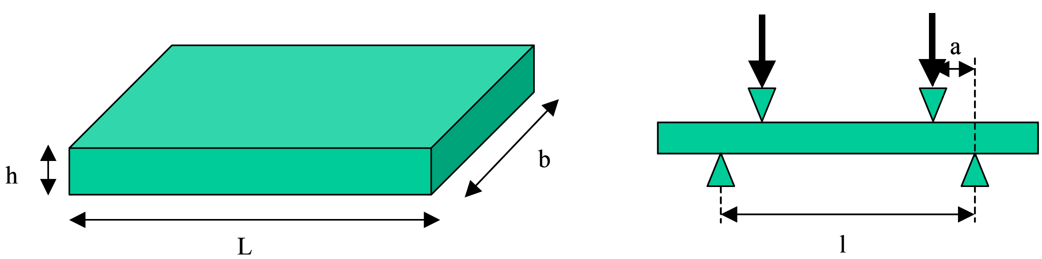


Fig. 2. Definition of the parameters used for the calculation of stress and sag for the four point bending tests

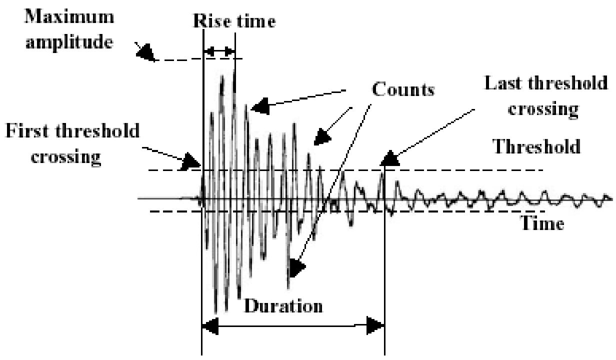


Fig. 3. Definition of the main shape parameters of an acoustic signal, from[4)]

predefined threshold and the maximal peak

- Number of counts: the number of alternations that the threshold is overshot
- Duration: the time between the first and the last overshoot of the defined threshold
- Energy: the integral of the squared signal over the duration of the salve

3. Results

The stress-sag curves of the oxidized steel sollicited in the four point bending test apparatus at 700°C and 900°C are presented on Fig. 4 and 5 respectively. The SEM observations of cross-sections for both cases (Fig. 4 and 5) show that the oxide scale presents cracks perpendicular to the metal / oxide interface which cross the whole oxide scale when the oxidized steel is sollicited at 700°C (Fig. 4) and that the damages are limited to a decohesion of the top part of the oxide scale when the system is sollicited at 900°C (Fig. 5). Concerning the stress-sag curves, it appears small discontinuities in the stress increase at 700°C (Fig. 4), and a strong decrease of the stress is observed at 900°C when the sag equals about 0.06 mm. So the evolution of the stress with the sag seems to depend on the kind of damage which appear in the oxide scale. In order to verify that the damages observed with the cross-sections occur during the four point bending, the acoustic emission signal recorded during the four point bending test is analyzed. Fig. 6 gives the energy of the acoustic emission salves as a function of their duration for both cases. On these diagrams, each point correspond to a discrete acoustic event. When the four point bending test occurs at

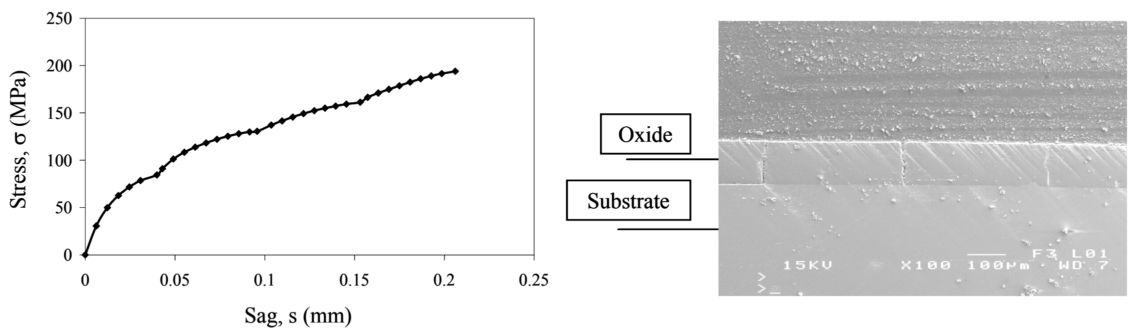


Fig. 4. Stress-Sag curve and SEM view of a cross-section of the steel oxidized at 900°C under a N_2+H_2O mixture, and sollicited at T=700°C

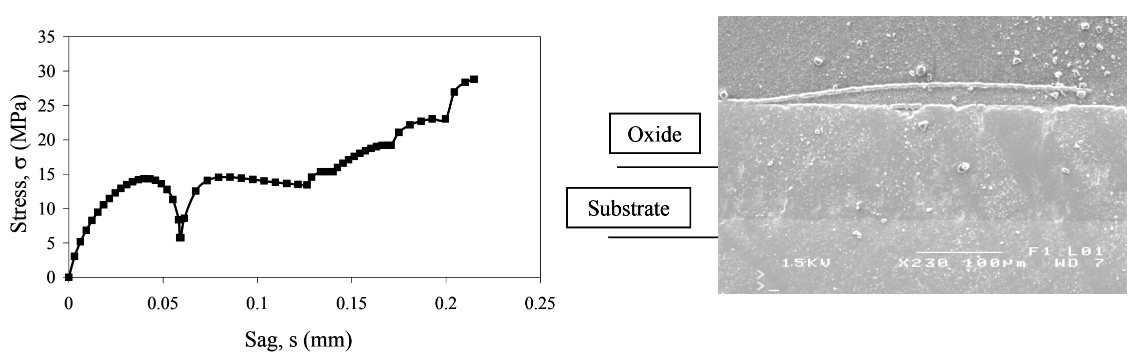


Fig. 5. Stress-Sag curve and SEM view of a cross-section of the steel oxidized at 900°C under a N_2+H_2O mixture, and sollicited at T=900°C

900°C, Fig. 6a shows that the number of events is limited as there are only a few points on the diagram. But the relatively high energy of some acoustic salves means that these acoustic events are clearly related to the delamination of the top part of the oxide, as observed on the cross-section of Fig. 5. When the mechanical test is performed at 700°C, the number of acoustic events is really higher. The energy values are also relatively high which allows to relate the acoustic signals to the propagation of the cracks.

In order to qualify the effect of humidity, the same experiments have been performed with only one difference in the experimental procedure: the step which corresponds to the 9 minutes of oxidation at 900°C under the wet atmosphere (N_2+H_2O) is replaced by an annealing step at 900°C during 9 minutes under dry nitrogen. The stress-sag curves, SEM observations of the cross-sections and acoustic emission diagrams are presented on Fig. 7 for the four point bending test performed at 900°C and on Fig. 8 for the mechanical test performed at 700°C. For both cases, no crack appear in the scale, perpendicularly to the metal/oxide interface, but decohesion of the scale at the metal/oxide interface occurs. Such an interfacial delamination occurs along all the interface when the sample is bended at 700°C (Fig. 8); moreover, in this case, there is a partial delamination between the outer and the inner part of the scale. For the mechanical test performed at 900°C, the interfacial delamination is discontinuous and occurs locally (Fig. 7). The acoustic emission diagrams show high energetic events which proves the occurence of the delamination during the mechanical test. The number of acoustic events is higher at 700°C which is in good agreement with the total delamination of the scale at this

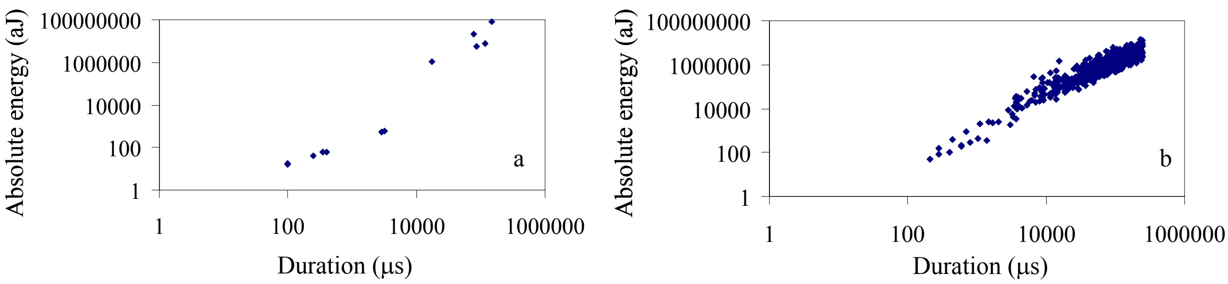


Fig. 6. Acoustic emission diagrams (absolute energies of the acoustic events versus their duration) for the steel oxidized under the N_2+H_2O mixture at 900°C, and sollicited (a) at 900°C and (b) at 700°C

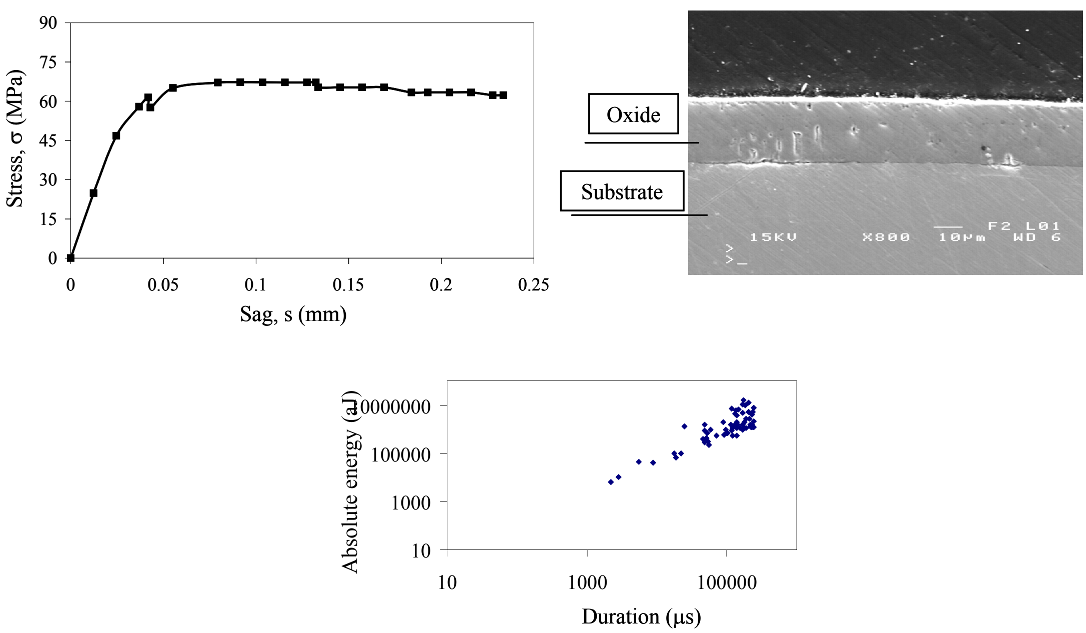


Fig. 7. Stress-Sag curve, acoustic emission diagram and SEM view of a cross-section of the steel oxidized at 900°C under a dry N_2, and sollicited at T=900°C

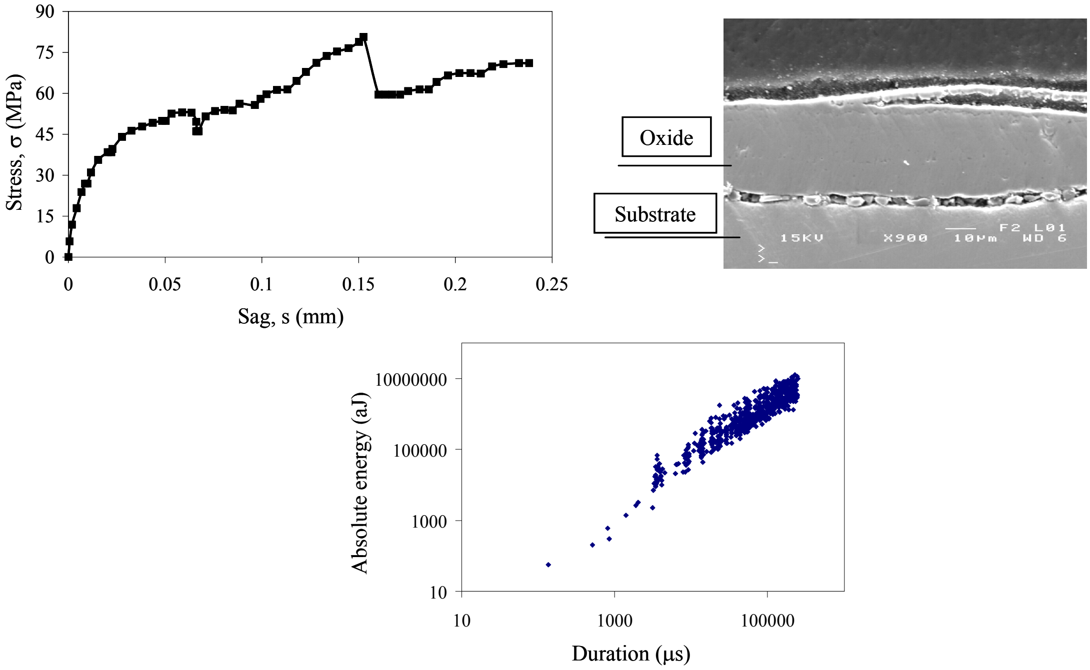


Fig. 8. Stress-Sag curve, acoustic emission diagram and SEM view of a cross-section of the steel oxidized at 900°C under a dry N_2, and sollicited at T=700°C

Table 2. Thicknesses of the oxide scales measured from he SEM cross-sections of Fig. 4, 5, 7 and 8

Temperature of the four point bending test [°C]	9 minutes annealing under dry N_2 [μm]	9 minutes annealing under N_2+H_2O mixture [μm]
700	30	110
900	23	137

temperature. The stress-sag curves are also in good agreement with these observations as only very small accidents are oberserved at 900°C, when only local delamination occurs. At 700°C the high stress decrease observed when the sag equals to about 0.15 mm is probably due to the total delamination of the scale at the metal/oxide interface.

From the SEM observations of the cross-sections of the oxidized samples, it is possible to measure roughly the thicknesses of the scales for the four cases presented above. Such scale thicknesses are given in Table 2.

4. Discussion

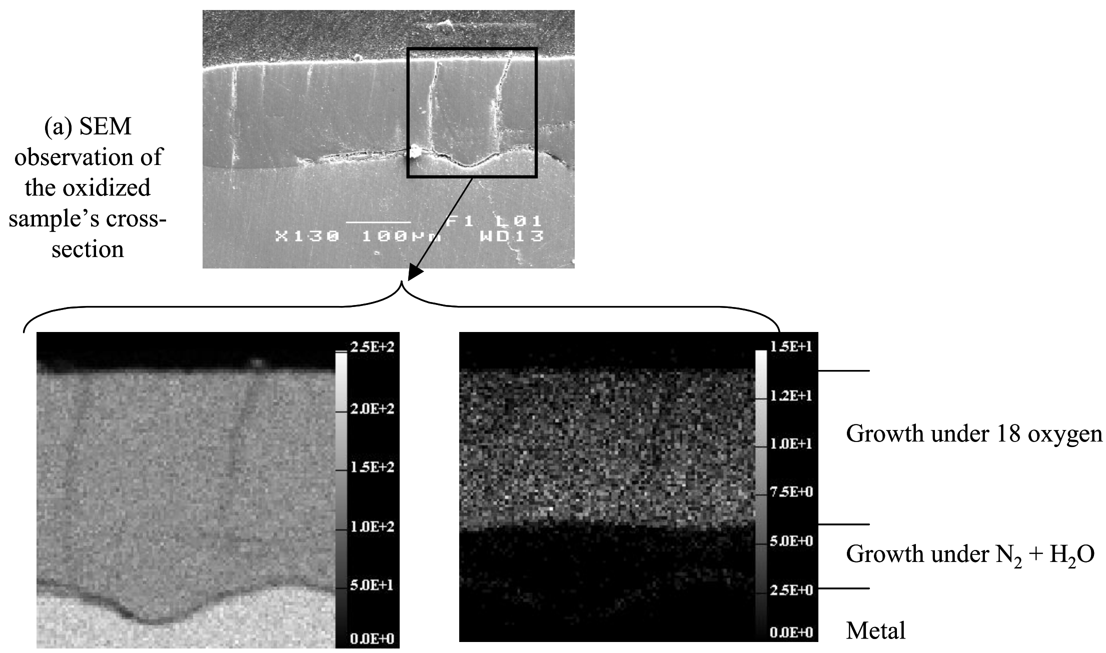
The obervations of the samples after experiments show that every cases lead to the growth of an oxide scale on the uncoated surface of the steel. The use of dry nitrogen does not avoid the oxide scale growth, even if the oxygen partial pressure is reduced in such an atmosphere. But the measured thicknesses clearly show that the use of N_2+H_2O mixture during the 9 minutes annealing at 900°C lead to thicker scales than the ones obtained when the experiments are totally performed under dry nitrogen (Table 2). Such an observation is evident because of the most oxidant nature of the N_2+H_2O mixture compared to dry nitrogen. From the present results, it is actually difficult to discuss only the effect of humidity itself. Other results show that in similarly conditions, for the same mild steel, the oxidation rate is greater in wet atmosphere than in dry air.[5)] On the other hand, some results obtained on pure iron at lower temperatures show that dry oxygen leads to faster oxidation growth than wet atmosphere.[6),7)] Actually the effect of water vapor itself on the growth rate is not clear, and depends on many factors (temperature, alloying elements, O_2/H_2O ratio, ···) which does not allow to adress a general behavior.

Concerning the mechanical damages of the scales, the experiments performed with the 900°C annealing under wet atmosphere lead to oxide scales which stay adherent to the substrate whatever the temperature is during the mechanical test. On the other hand, scales which have grown without steam, exhibit delamination at the metal/oxide interface. Such a delamination is discontinuous along the interface when the mechanical test is performed at 900°C, and the scale is totally separated of the substrate after the mechanical test performed at 700°C. It thus appears that the scale adherence to the substrate is promotted by the presence of a wet atmosphere during the 9 minutes annealing at 900°C. It is interesting to note that the general tendency described in the literature is that the adherence at the metal/oxide interface decreases when the scale thickness increases,[8] and that the scale adherence is better when the oxidation is performed under wet atmosphere.[2] The experiments performed in the present study lead to a competition between these two tendencies as the oxide scales which grow under wet atmosphere are about four times thicker than the scales obtained under dry atmosphere. The results show that the effect of the humidity is more important than the effect of the scale thickness on the adherence of the oxide in the present conditions.

When the 9 minutes annealing is performed under the N_2+H_2O mixture, the scale damage is limited to a decohesion of the top part of the oxide scale when the system is sollicited at 900°C (Fig. 5). When the four point bending point is performed at 700°C, cracks are present through the whole oxide scale, perpendicularly at the metal / oxide interface. Actually, during the annealing step at 900°C, the oxide scale is mainly formed by an inner part of wustite (FeO) mounted by a thinner layer of magnetite (Fe_3O_4) and finally, a very thin layer of hematite (Fe_2O_3) at the external part of the scale.[9),10)] Wustite represents around 95% of the scale thickness for oxidation in air in the temperature range 700-1250°C.[11] The existence of these three phases has been observed event for very short oxidation duration (less than 1 s).[12] At 900°C, the three oxide phases exhibit a ductile mechanical behavior. When the sample is cooled down to 700°C, the brittle/ductile transition temperature is crossed for FeO and Fe_3O_4, so the oxide scale becomes mainly brittle.[13),14)] This could explain that when the mechanical loading is performed at 700°C, the oxide scale has greater difficulties to follow the metal deformation than at 900°C, and the oxide scale is damaged by through scale cracks. Such a behavior which demonstrates that the ductile/brittle temperature transition for the oxide scales obtained on mild steels is between 700 and 900°C is in agreement with other works; Picque[15] finds that this temperature lies between 700 and 800°C from high temperature four point bending tests, and Krzyzanowski et al[1),16)] obtain a brittle/ductile transition at 860°C for oxide scales on a mild steel with high temperature tensile tests.

Another reason which could explain the occurence of strongest damages at 700°C than at 900°C is the appearance of thermal stresses due to the temperature change. These stresses have been calculated;[17] the value of the thermal stresses is 65 MPa when the temperature changes from 900°C to 700°C. Such stresses could help for the crack propagation through the oxide scale.

For the two cases which lead to delamination of the



(b) RBS Signal of iron (c) NRA signal of O18

Fig. 9. SEM cross-section observation and corresponding chemical analysis by a nuclear microprobe of a sample annealed 9 minutes under N_2+H_2O at 900°C, sollicited at 900°C and annealed 2h under $^{18}O_2$ at 900°C

scale at the metal / oxide interface (Fig. 7 and 8), the scale delamination is more important when the four point bending test is performed at 700°C than at 900°C. As mentionned above, the occurence of more important damages at the lower temperature of the mechanical test could be explained by the decrease of the scale plasticity between 900 and 700°C. In the present case (9 minutes annealing under dry N_2), the nature of the scale damages during the bending test performed at 700°C, could be either through scale cracks because the oxide scale is brittle, either the scale delamination at the metal/oxide interface because of the weak adherence of the scale under dry atmosphere. In the present case, only the scale delamination has been observed.

Finally, from the results presented here, one notes that the acoustic emission does not allow to differentiate between crack propagation in the scale and scale delamination (a thin signal analysis could be useful to perform such a differentiation). Thus the post-mortem observations of cross-sections by SEM are still necessary to be sure of the damage nature. Moreover, during this study, many other experimental conditions have been used. The acoustic characteristics of the damages was not so clear at the beginning of the work, and the SEM observations were not sufficient because the eventually observed damages could be developped during cooling and not during the hot four point bending test. Then it was decided to introduce oxygen 18 for 2 hours after the four point bending, before cooling:

- If cracks exist, then they will be filled by a new oxide developped under oxygen 18.
- In case of delamination at the metal / oxide interface, a new oxide scale will be developped closed to the metal with the oxygen 18.
- If no damage appear during the bending test, the 18 oxygen will only lead to the normal growth of the oxide scale by cationic diffusion mechanism; the new oxide forms the external part of the scale

Fig. 9 is an example of such an analysis. The SEM observation of the sample cross section show that cracks and local delamination are present in this case which acoustic emission diagram didn't present any high energy signal during the four point bending test. The chemical analysis has been performed by nuclear microprobe analysis (RBS for the iron and NRA for he oxygen 18).[19] The oxygen 18 is placed only in the external part of the scale and the location of the cracks does not correspond to a special repartition of the oxygen 18. Then, this analysis of the oxygen 18 shows that the observed damage didn't occur before or during the annealing step under oxygen 18. So they occur during the final cooling.

5. Conclusion

The main result of the present study concerns the effect of water vapor which promotes the adherence of the iron oxide scales grown at 900°C under wet atmosphere on mild steels. This result is based on four point bending tests performed at 700 and 900°C. When the mechanical tests are performed at 700°C, whatever the oxidant atmosphere is, the oxide scales are more brittle than at 900°C. When the scale has grown under wet atmosphere, these damages are through scale cracks, perpendicular to the metal/oxide interface. When only dry atmosphere is used, the scale sollicited at 700°C is both brittle and weakly adherent to the substrate. Then the type of damages (delamination or through scale cracks) could potentially occur. In the results presented in this paper, only delamination is observed in this case and there probably exists a competition between cracking and scale decohesion. Thus a weak change on the test conditions could eventually lead to scale cracking instead of scale delamination (for instance, the quantity of a minor alloying element in the steel which could promote the oxide scale adherence on the substrate[18]).

Concerning the scale adherence, it was also shown that the promoting effect of water vapor is not counterbalanced by thicker oxide scales obtained under the wet atmospheres. In other words, the thickness of the scale which can act on its adherence to the substrate (an increase of the thickness generally lead to a worse adherence) is a minor effect compared to humidity in the present conditions.

From a technical point of view, the use of acoustic emission is proved to be usefull in order to detect in situ (in temperature and under controlled atmosphere) the occurence of damages during mechanical loading. The use of oxygen isotopic marking has been also mentionned as a possible way to know if the damages occur in temperature or during the final cooling.

References

1. M. Krzyzanowski and J. H. Beynon, Metal Forming Science and Practice, p. 259, J. G. Lenard (Ed.), Elsevier, Amsterdam, 2002.
2. B. Picque, Experimental study and numerical simulation of iron oxide scales mechanical behavior in hot rolling, p. 24, PhD thesis, Ecole des Mines de Paris, France (2004).
3. S. Frydman and A. Pszonka, *Materials Science and Engineering*, **40**, 191 (1979).
4. M. Boinet, S. Verdier, S. Maximovitch, and F. Dalard, *Surface and Coatings Technology*, **199**, 141 (2005).
5. J. Favergeon, A. Makni, G. Moulin and L. Lahoche,

Proc. of the Eurocorr Conference, Lisboa, Portugal (2005).
6. A. P. Grosvenor, B. A. Kobe, and N. S. McIntyre, *Surface Science*, **574**, 317 (2005).
7. S. J. Roosendaal, J. P. R. Bakker, A. M. Vredenberg and F. H. P. M. Habraken, *Surface Science*, **494**, 197 (2001).
8. P. Hancock and J. R. Nicholls, *Materials Science and Technology*, **4**, 398 (1988).
9. M. Torresa and R. Colas, *Journal of Materials Processing and Technology*, **105**, 258 (2000).
10. D. P. Burke and R. L. Higginson, *Scripta Materialia*, **42**, 277 (2000).
11. N. Birks and G. H. Meier, Introduction to High Temperature Oxidation of Metals, Edward Arnold, London (1983).
12. W. H. Sun, A. K. Tieu, Z. Y. Jiang, H. T. Zhu, and C. Lu, *Journal of Materials Processing and Technology*, **155**/156, 1300 (2004).
13. Y. Hidaka, T. Anraku, and N. Otsuka, *Oxidation of Metals*, **59**(1-2), (2003)
14. Y. Hidaka, T. Anraku, and N. Otsuka, *Materials Science Forum*, **369**-372, 555 (2001)
15. B. Picque, P. O. Bouchard, P. Montmitonnet, and M. Picard, *Wear*, **260**, 231 (2006).
16. M. Krzyzanowski, J. H. Beynon, and C. M. Sellars, *Metallurgical and Materials Transactions B*, **21B**, 1483 (2000).
17. G. Moulin, A. Makni, J. Favergeon, L. Lahoche, M. Viennot, and P. Berger, *Ceramics*, **92**, 89 (2005).
18. T. Asai, T. Soshirod, and M. Miyahara, *ISIJ International*, **37**, 272 (1997).
19. P. Berger, G. Moulin, and M. Viennot, *Nuclear Inst and Methods in Physics Research B*, **130**, 717 (1997).