THERMOGRAVIMETRIC DETERMINATION IN OXIDIZING AND/OR SULFIDIZING ATMOSPHERES OF THE BEHAVIOUR OF THE STEEL Fe 2,25 Cr 1 Mo EITHER UNCOATED OR SUPERFICIALLY ALUMINIZED

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SUMMARY

The behaviour of a ferritic steel (Fe 2,25 Cr 1 Mo) was studied in oxidizing and/or sulfidizing atmospheres. In SO_2 atmosphere and in a synthetic coal gazification sulfidizing atmosphere, paralinear kinetics occurred.

Aluminizing the steel by pack cementation with a chloride activator was shown to lead to the formation of a Fe_2Al_5 coating. This superficial aluminization protected well this steel from attack by the different atmospheres under consideration.

I - INTRODUCTION

Metallic materials used in the energy systems and turboengines show, during their service life, essentially two types of degradation :

- degradation of their mechanical properties, due to the high temperatures involved,

- degradation by corrosion due to the contact with hot gases.

Many studies have therefore been conducted these last years concerning the behaviour of alloys in oxygen and/or sulfur containing atmospheres in order to understand the corrosion mechanisms. The comprehension of the phenomena is indeed fundamental to propose solutions to the degradation processes.

This paper deals with the behaviour of a ferritic steel Fe 2,25 Cr 1 Mo in sulfur dioxide and in a typical coal gazification atmosphere. In order to improve the life time of the steel, its aluminization by pack cementation was envisaged.

II - THE MAGNETIC SUSPENSION MICROBALANCE

The corrosion kinetics of the steel was followed with a Sartorius magnetic suspension microbalance (Fig. 1).

This system allows precise measurements (10 μg) in very aggressive environments, as the weighing system is entirely separated from the reaction chamber (1). The transmission of the weight information involves two magnets. The top one is

suspended to the weighing system, and the sample hangs to the bottom one. These magnets are separated by a quartz window.
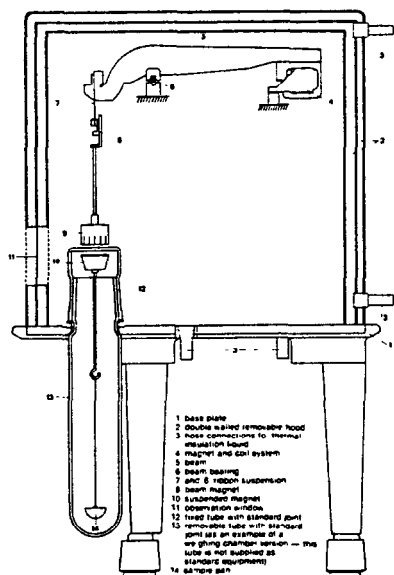

Fig. 1. Magnetic suspension microbalance. Design principle.

This apparatus involves two electronic systems :

- a suspension system allowing the bottom magnet to remain at a constant distance from the top magnet

- a measuring system, consisting of a coil acting on the beam of the balance. The balance is continuously maintained in equilibrium by the coil and the current flowing through the coil is continuously recorded. Its variations are proportional to the weight changes.

The thermal regulation of the balance must be very accurate to avoid changes in the base line. A water-jacket with water flowing at 40 °C keeps the temperature within ±1°C.

When the vacuum achieved in the reaction chamber is in the order of 1×10^{-5} torr, the furnace is turned on. When the temperature is stabilized, the reactive gases are introduced. The experiments are performed either in static atmosphere of pure SO_2 or in dynamic atmosphere (coal gazification type).

At the end of the experiment, the sample is cooled down under vacuum, then analysed by X-ray diffraction, optical or electronic microscopy and energy dispersive analysis.

III - EXPERIMENTAL RESULTS

III - 1. Behaviour of the Fe-2,25 Cr-1 Mo steel in oxidizing   and/or sulfidizing atmospheres

III - 1.1. SO_2 atmosphere

Kinetical aspects

The reaction of the steel with SO_2 was followed between 400 and 500°C under 100 torr pure SO_2.

In Fig. 2, several kinetical curves observed at different temperatures are presented. The kinetical regime is paralinear. No pressure influence was detected between 10 and 400 torr.

The steel exhibits a better behaviour in SO_2 than pure iron. The kinetical regimes are similar, but the rates very different.
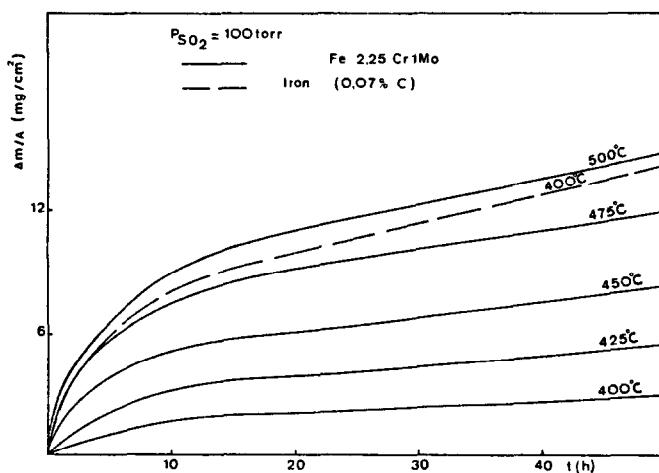

Fig. 2. Oxidation of the Fe-2,25 Cr-1 Mo in 100 torr pure SO_2. Weight gain vs time curves at different temperatures. The curve for pure iron oxidation in this atmosphere is given as a comparison.

Formed products and morphology of the corrosion scale

In all the temperature range, X-ray diffraction showed that the scale contains Fe_2O_3, Fe_3O_4 and $Fe_{1-x}S$. No chromium or molybdenum-containing compound was identified.

Microscopic examinations showed that the corrosion scale contains two subscales (Fig. 3). Microprobe measurements detected the presence of the elements S, O and Fe in both subscales. Cr^{3+} ions are probably substituted to Fe^{3+} ions in magnetite (2). Glow discharge spectrometry profiling confirmed these results (fig 4).
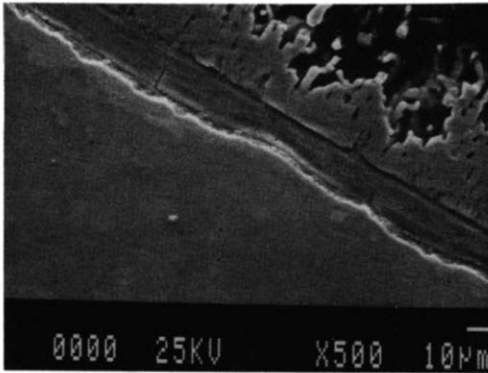
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Fig. 3. Cross section of a sample oxidized
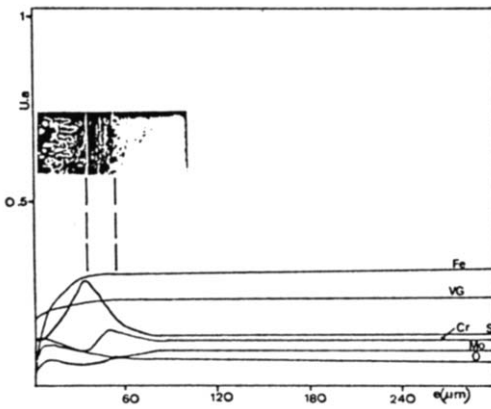for 50h in 100 torr SO_2 at 450°C.

Fig. 4. Glow discharge spectrometry profiles
of the different elements. Sample as in Fig. 3.

The corrosion scale can be therefore schematically described as follows (Fig. 5) :
- an internal subscale, in contact with the alloys, containing a mixture $(Fe,Cr)_3O_4$
and $Fe_{1-x}S$
- an external subscale containing Fe_2O_3 and $Fe_{1-x}S$

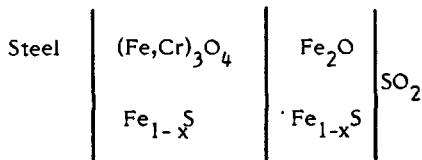| Steel	$(Fe,Cr)_3O_4$	Fe_2O	
	$Fe_{1-x}S$	$Fe_{1-x}S$	SO_2

Fig. 5. Distribution of the compounds in the corrosion scale

EDAX analysis has detected a difference in the sulfur content of the two subscales. The external subscale contains three times more sulfur than the internal one (table 1).

TABLE 1

Ratio $\frac{\text{area of sulfur peak}}{\text{area of iron peak}}$ obtained by EDAX

internal scale	External scale
0,2098	0,5154

Observations made at different times show that the thickness of the internal subscale stops growing when the kinetical curve becomes linear. A similar observation was made during the oxidation of the same steel in oxygen (3).

III - 1.2. Coal gazification type atmosphere(CGA)

Kinetical aspect

The experiments were performed in flowing gas. In Fig. 6 are presented the kinetical curves obtained when the Fe-2,25 Cr-1 Mo is maintained at different temperatures with the following atmosphere (vol %) : H_2 40 %, CO 30 %, CO_2 20 %, CH_4 8,3 %, H_2S 1,7 %.

The kinetical curves are paralinear, in all the 500 - 600°C temperature range.
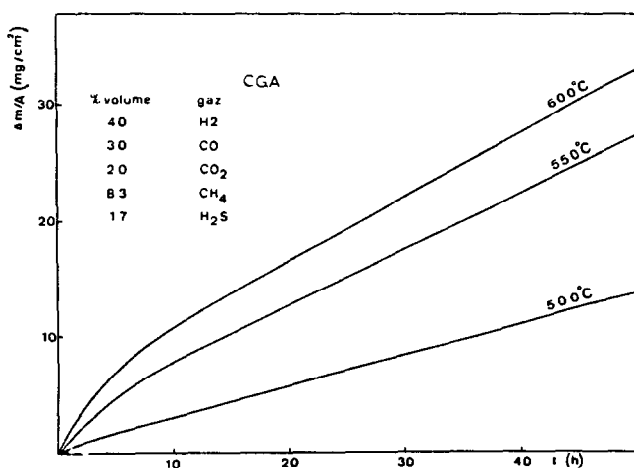

Fig. 6. The behaviour of the Fe 2,25 Cr-1 Mo in the coal gazification atmosphere. Weight gain vs time curves at different temperatures

Formed products and morphology of the corrosion scale

Only sulfides were identified by X-ray diffraction. $Fe_{1-x}S$ was the main product of the scale which contained also CrS. No oxide was present in this scale.

As seen in Fig. 7 the corrosion scale contains two subscales
- an internal one, containing $Fe_{1-x}S$ and CrS
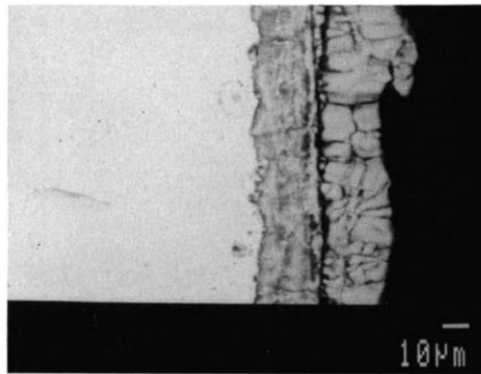- an external one, containing only $Fe_{1-x}S$.

Fig. 7. Cross section of a sample corroded for 50h
in the coal gazification atmosphere at 500°C.

III - 2. Behaviour of the aluminized Fe-2,25 Cr-1 Mo steel in oxidizing or/and sulfidizing atmospheres

III - 2.1. Aluminization of the samples

The pack cementation technique was used. The samples were embedded in a mixture of powders containing 40 Wt % Al, 55 Wt % Al_2O_3, 5 Wt % NH_4Cl, heated under inert gas. The retained temperature was 800°C and the time of cementation was 3 h. In these conditions, a 30 μm surface layer of Fe_2Al_5 forms on the steel (Fig. 8).

III - 2.2. Corrosion in SO_2

The kinetics of oxidation of the aluminized steel were followed between 900 and 1000°C under 100 torr of static SO_2. As seen in Fig. 9, the kinetics are parabolic. No pressure influence was detected.
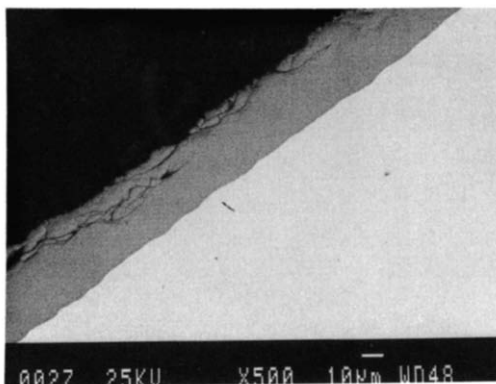
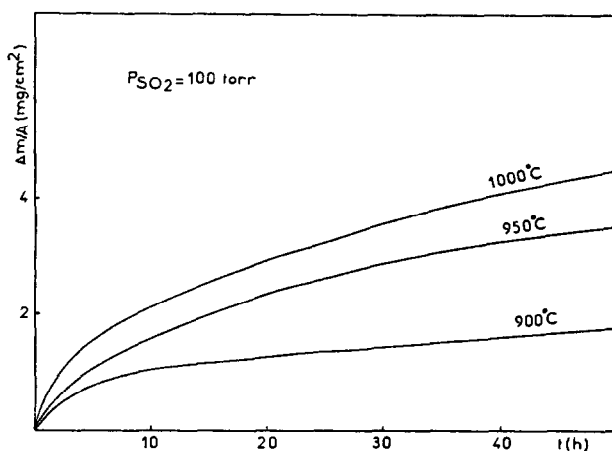Fig. 8. Cross section showing the coating formed by pack cementation

Fig. 9. kinetical curves for the corrosion of coating by SO_2

The only formed product by the reaction was αAl_2O_3. No sulfide was observed contrary to what occured on the uncoated steel. Evidence of the dissolution of the coating in the matrix during the corrosion test was assessed by the presence of the Fe_3Al and FeAl diffraction lines.

Energy dispersive analysis confirmed the only presence of alumina in the scale.

III - 2.3. Corrosion in the coal gazification atmosphere

Experiments were conducted in flowing gas, with the same composition as above. In Fig. IO it may be seen that the rate law is linear after a short parabolic period . The rate of the linear law is lower than the slope of parabola at the transition point. This result is comparable to what was observed during oxidation of the non aluminized steel in O_2 (3).
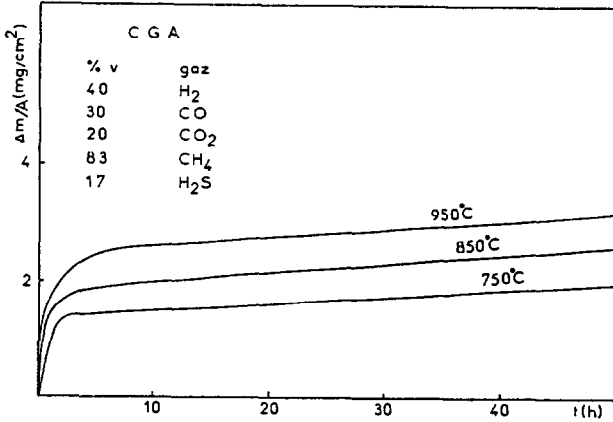

Fig. 10. Kinetical curves for the corrosion of the coating by a C G A.

Under 950°C, no crystallized compound was detected by XRD. Amorphous alumina formation was probably responsible for the weight changes observed. At 950°C and above, αAl_2O_3 appears, concurrently with the FeAl and Fe_3Al lines.

Energy dispersive analysis confirmed the presence of alumina and the Al-depletion in the inner part of the coating, corresponding to the subaluminides.

IV - DISCUSSION

IV - 1. Corrosion of the non aluminized steel in SO_2

Thermodynamic

The phase stability diagram of the Fe - Cr- Mo - O - S system was drawn using thermodynamical values from JANAF (4,5,6) and BARIN (7). The 700 K diagram is presented in Fig 11. Point A corresponds to the initial S_2 and O_2 pressures in the gas phase obtained by the calculation where SO_2, S_2O, SO and SO_3 are taken into account (8). It can be seen that the stable compounds in contact with the gas are $FeSO_4$, MoO_2 and Cr_2O_3. The absence of ferrous sulfate in the scales formed at this temperature shows that equilibrium is not reached at this interface.
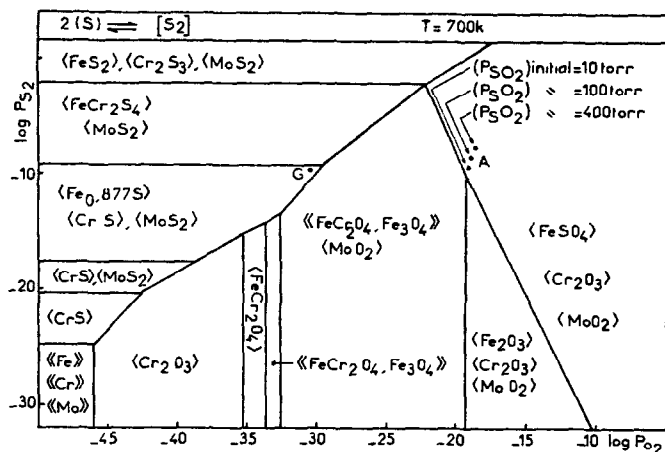
Fig. 11. Stable condensed phases in the system Fe-Cr-Mo-0-S.

In contact with the alloy, CrS or Cr_2O_3 is the stable compound. None of these products were observed and this fact may be the consequence of the solubility of chromium in magnetite.

Diffusion   processes

Several experiments, using marker experiments have shown that the corrosion scale grows by both cationic and anionic transport • Two types of diffusionnal fluxes are therefore responsible of the weight changes :

-iron cations diffusing outwards

- oxygen and sulfur diffusing inwards, either separately or simultaneously in SO_2 molecules. It is known that many authors propose this last hypothesis (9 - 10). In the present case, this has not to be envisaged as the sulfur partial pressure in the atmosphere is higher than the FeS/Fe equilibrium pressure (P = 2.5 x 10^{-18} bar at 700 K).

It was seen that the sulfur content in the internal part of the scale is less than in the external part. This observation agrees with the hypothesis of sulfur and oxygen separate diffusion.

Kinetics

During the parabolic period, two types of diffusion are involved in the growing of the scale :

- the outward diffusion of iron ; this process is probably not rate limiting , as the equilibrium is not reached at the external interface. This contribution must lead to a linear growing.

- the inward diffusion of sulfur and oxygen, through the overall scale. Due to the presence of chromium , the internal subscale acts probably as a barrier layer. Its growing is therefore parabolic.

The overall rate law is therefore the sum of both mechanisms.

After about 20h, the internal subscale stops growing and the rate law, controlled only by the external interfacial reaction, becomes linear. The origin of this phenomenon is probably the healing of microcracks, but was not clearly elucidated.

This mechanism should exhibit an influence of SO_2 pressure. It must be however observed that no simple dependance relation exists between P_{SO_2}, P_{O_2} and P_{S_2}. It is therefore impossible to predict whether the P_{SO_2} influence should be important or not.

IV - 2. Behaviour of the steel in the coal gasification atmosphere

Thermodynamics

On the phase stability diagram of the Fe-Cr-Mo-O-S system, the point G describes the theoretical oxygen and sulfur partial pressures in the coal gasification type atmosphere. This atmosphere is seen to be only sulfidizing for the system studied. Only $Fe_{1-x}S$, CrS and MoS_2 are stable in contact with it. MoS_2 was never observed in the corrosion scales, probably due to its very low amount in the steel.

Morphological studies have shown that the internal subscale contains Fe_{1-x} and CrS, and the external subscale only $Fe_{1-x}S$. This observation leads to the conclusion that both sulfur and iron diffuse in the scale. Sulfur diffusion participates in the internal growing of the mixed $Fe_{1-x}S$ /CrS subscale, iron participates in the external growing of the $Fe_{1-x}S$ subscale.

Kinetics

The corrosion proceeds according to a parabolic initial period ($\sim$10 hours)followed by a linear regime. The internal subscale stops growing when the rate law changes from parabolic to linear. As similar observations were made in the case of the oxidation of the same steel by pure SO_2, we propose that the same mechanism is involved here (see § Iv-1).

IV - 3. Corrosion of the aluminized steel in SO_2

The Fe-Al-O-S diagram drawn at 1200 K (Fig. 12) shows that $FeAl_2O_4$ is the stable compound in contact with the gas. Al_2O_3 is only stable in contact with Fe_2Al_5.
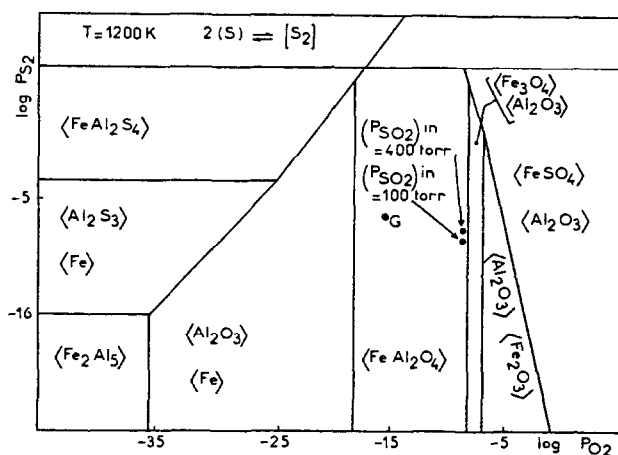
Fig. 12. Stable condensed phases in the system Fe_2Al_5-O-S.

The absence of $FeAl_2O_4$ in the corrosion scale confirms that S and Fe do not largely diffuse within Al_2O_3.

The alumina grows probably by inward oxygen diffusion. The rate limiting step is probably the transport of oxygen across the alumina scale, leading to parabolic kinetics.

IV - 4. Behaviour of the aluminized steel in CGA

In the $Fe_2 Al_5$ - O - S phase stability diagram, the point G describes the gas phase composition (Fig. 12). The stable compound in equilibrium with the gas is therefore $FeAl_2O_4$. As this compound was never observed, it may be concluded that iron does not diffuse through the alumina formed in contact with the steel.

Two mechanisms can explain the observed rate law :

- a change in the texture of the alumina scale, leading to an enhanced protective character

- a change in the interfacial CO_2 adsorption or decomposition rate (or CO desorption rate) with the coverage of the substrate with alumina (diminution of the catalytic effect of the steel).

V - CONCLUSION

The steel Fe-2,25 Cr-1 Mo corrodes in SO_2 more rapidly than in oxygen . The kinetics are paralinear. Many authors envisage the diffusion of SO_2 within the scale as a necessary process. In the present case, this has not to be taken into account, as the sulfur partial pressure in the gas is sufficient to allow the formation of FeS.

In a C G A type, the FeS and CrS formation follows a paralinear law. Sulfur and iron both diffuse in the corrosion scale.

The superficial aluminisation of the steel by pack cementation was shown to improve greatly the behaviour of the steel in either the atmospheres. In this case, an alumina scale is responsible for the observed protection.

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