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## Influence of Sulphur and Phosphorus on the Hot Deformation of Fe-Cr 13% High Purity Steel

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**Abstract :** A series of Fe-Cr13%-C high purity steels containing increasing volume fractions of Sulphur (30, 60 and 100ppm) and Phosphorus (30, 60 and 100ppm) were prepared in order to study their hot deformation properties by tensile tests at various strain rates ( $10^{-1}s^{-1}$  to  $10^{-4}s^{-1}$ ) and at temperatures from 700°C to 1100°C. It is observed that the hot ductility is lowered at 1000°C with the addition of sulphur. However, this decrease is relatively small (about 30% for 100ppm of sulphur) and quite similar for all additions of sulphur. When phosphorus is added, the embrittlement is along the whole deformed specimen. The usual criteria of ductility by parameter Z do not seem to be sufficient to describe this embrittlement.

### 1. INTRODUCTION

Hot working of metals is current metallurgical practice. However, it is usually limited by a decrease in ductility in a wide temperature range where the occurrence of defects produces superficial or internal fractures. In industry, these damaging defects appear in the bending process during solidification in continuous castings of slabs and billets, or during hot rolling [1], hot forging [2], etc. Due to the difficulty of studying the influence of elements in industrial steel [3], pure metals with additions of a controlled quantity of trace elements, are usually prepared and deformed in order to characterize their hot workability and optimize the design of controlled deformation schedules.

Some researchers [4, 5, 6, 7] have then shown that the decrease in ductility of microalloyed steels is essentially due to hardening precipitates in the matrix as well to grain boundary segregation of embrittling elements.

In the case of sulphur, brittleness is not affected by this trace element if its level is lower than 30ppm as cavities initiated in the boundaries are isolated in the grain. However, brittleness increases when the sulphur content is higher than 60ppm and sulphur segregates at grain boundaries, facilitating the propagation of fractures. Addition of phosphorus seems to give analogous results [8].

It was with this in mind that two types of stainless steel with 13%Cr (ferritic and martensitic) were prepared with controlled additions of sulphur (0 ppm to 100ppm) or of phosphorus (0 ppm to 100ppm) and deformed by tensile tests at temperatures varying from 700°C to 1200°C, and at strain rates of  $10^{-3}s^{-1}$  and  $10^{-4}s^{-1}$ . Results show that hot ductility decreases if sulphur and phosphorus are added separately. However, this decrease is small. Moreover, it does not seem to depend on sulphur concentration. On the other hand, with the addition of phosphorus, the embrittlement is distributed along the whole sample and the usual Z criterion (reduction in area) does not seem to be sufficient to describe such behaviour.

### 2. EXPERIMENTAL.

#### 2.1 Preparations of high purity Fe-13%Cr alloys doped with sulphur and phosphorus

Two high purity alloys (Fe-13%Cr) of martensitic stainless steels with 0.2%C and ferritic stainless steels with 0.02%C were prepared. They were then doped with sulphur and phosphorus.

Preparations of high purity iron and chromium were obtained from the Laboratory of the School of Mines of Saint Etienne (France). They were prepared by zone melting, in an argon controlled atmosphere, in a boat-shaped silver crucible. Homogeneity was controlled by  $\gamma$  source spectrometry and emission spectroscopy analysis.

Contents of trace elements (sulphur or phosphorus) for the two types of Fe-13%Cr-C alloys were equal to : 30, 60 et 100ppm for both elements.

The prepared alloys were then hot forged (1150°C) by power hammering in order to obtain testing bars which were hot formed (950°C) into cylindrical bars with diameter of 8.8mm by rotary hammering with a reducing machine. Test pieces were machined for hot deformation by tensile testing after segregation heat treatment. These heat treatments consist of a quenching after a homogeneous treatment as an austenized heat treatment at 1100°C for 30mn followed by segregation annealing at 700°C for 60mn in argon. Samples were cooled in the furnace to ambient temperature.

## 2.2 Hot deformation

Tensile tests were used to study the deformation behaviour of our alloys and the ductility evolution with temperature. The criteria for ductility were the parameter of area reduction  $Z$  at rupture and defect density ( $A_p$ ), measured by image processing.

The deformation machine used [9] performs tensile tests in an argon atmosphere and quenching of deformed specimens. Deformations were carried out in temperatures ranging from 700 to 1200°C (figure 2) after heat treatment to effect maximum precipitation of carbides and segregation of sulphur or phosphorus.

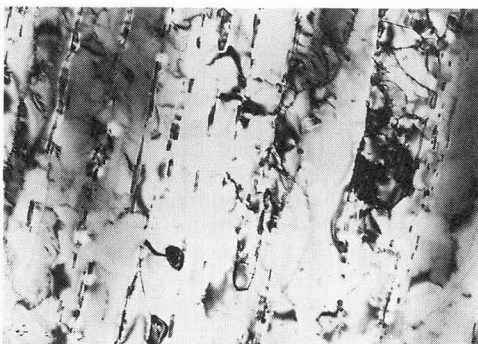
## 3. EXPERIMENTAL RESULTS

### 3.1 Non deformed samples

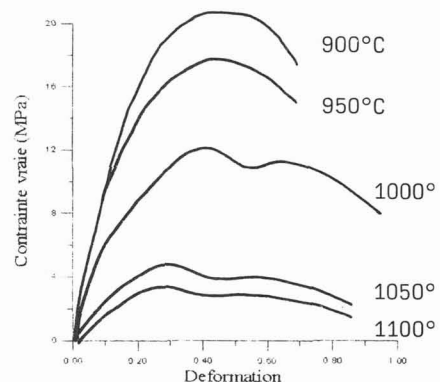
Critical points were determined by dilatometry. It is seen that 0.02% C alloy does not present any singular point during heating or cooling. On the other hand, 0.2% C alloy has two transformation points around 810°C during heating and 320°C ( $M_s$ ) during cooling.

Hot deformation tests between 700°C and 1200°C were then carried out in the austenitic domain for 0.2% C alloy and in the ferritic domain for 0.02% C alloy.

X rays diffraction confirm these results and reveal also the presence of  $M_{23}C_6$  carbides precipitates. These very fine precipitates were also observed with Transmission Electron Microscopy at very high magnification (Figure 1).



**Figure 1:** Carbide precipitates ( $M_{23}C_6$ ) observed by Transmission Electron Microscopy. 0.2% C alloy x 200 000



**Figure 2:** True stress-strain curves  $\sigma(\epsilon)$  Fe-13Cr-0.2C-0.003S

### 3.2 Hot deformed samples

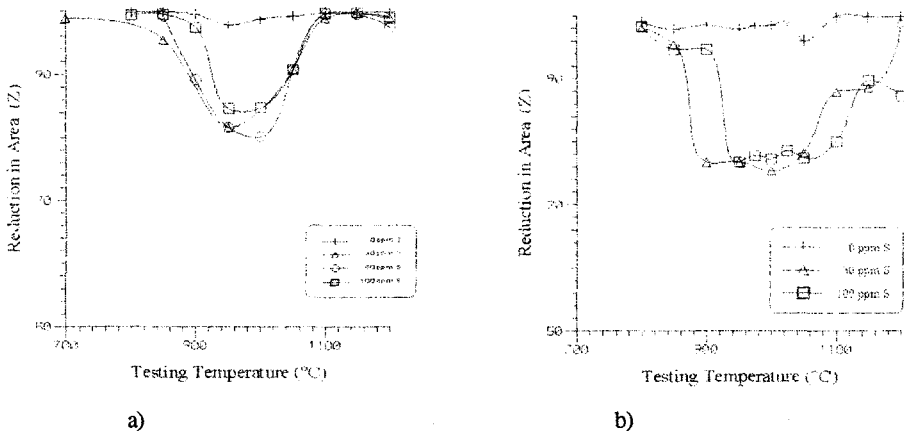
Experimental true stress-strain curves  $\sigma(\epsilon)$  are presented in figure 2. It can be seen that the value of the maximum tensile stress is low (under 30 MPa) and necking is achieved at low stresses.

Above the temperature 950°C, sinusoidal variations in  $\sigma(\epsilon)$  are observed clearly indicating the presence of dynamic recrystallisation liberated from precipitate dissolution in the case of martensitic steels (Fe-13%Cr-0.2%C). However, in the case of ferritic steels (Fe-13%Cr-0.02%C), no variations are seen even at elevated temperatures confirming a probable dynamic restoration.

Examination of  $\sigma(\epsilon)$  curves at different deformation temperatures for all alloys doped with sulphur or phosphorus shows that the increase of temperature has an effect of decreasing slightly elongation of alloys.

#### 3.2.1 Influence of sulphur

The dependence of ductility on temperature is represented by variation of the coefficient  $Z$  (%) in figures 3a and 3b for sulphur doped alloys in the ferritic and austenitic phases respectively. It can be seen that the trough observed is small and does not vary with sulphur content in the two alloys ( $Z \cong 80\%$ ). In the case of the 0.02%C - alloy, the lower ductility is obtained at 950°C. However, for the 0.2%C-alloy, the minimum is extended from 850°C to 1050°C.



**Figure 3:** Evolution of area reduction at rupture at  $\epsilon = 2.10^3 \text{ s}^{-1}$  sulphur doped alloys  
 (a) 0.02 %C alloy (b) 0.2 %C alloy

This observed small effect is unexpected as all previous work mentions a large decrease in ductility after sulphur segregation [7]. It seems then that in Fe-13%Cr stainless steel, sulphur does not play a significant role in embrittlement. Observations by scanning electronic microscopy of deformed samples show that cavitation phenomena are predominant being related to diffusion processes.

Revealed fractures are intragranular and ductile with presence of voids for the alloys with 30ppm content sulphur. However, they are intergranular, with sharp planar facets for high levels of sulphur (100ppm). For intermediate sulphur levels (e.g. 60ppm), fractures are of mixed types.

This mechanism of embrittlement is usually found for deformed microalloyed steels doped with sulphur. In fact, intergranular embrittlement due to sulphur segregation at the grain boundaries has been observed in pure iron doped with 50ppm of sulphur [7]. When deformed at high temperature, competition occurs between the above process and dynamic recrystallisation.

Increasing the temperature above 1000°C revives ductility since segregation at the grain boundaries is lower above the sulphur solubility temperature [10]

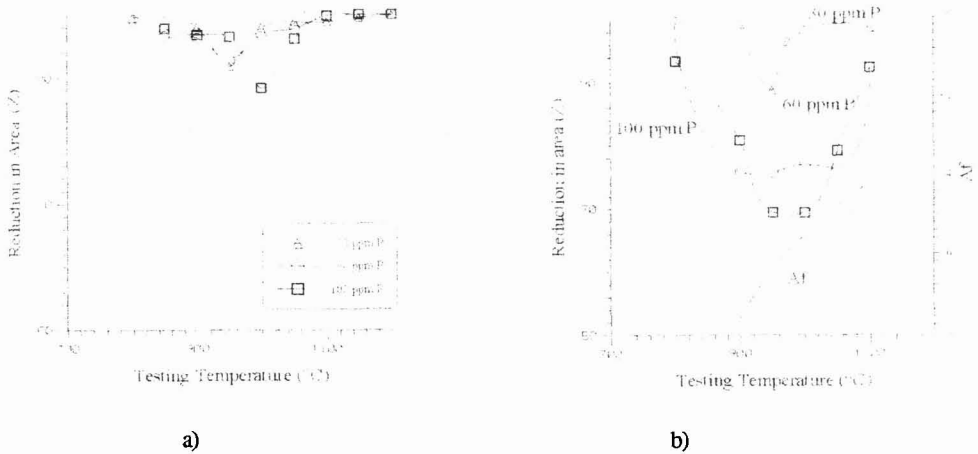
#### 3.2.2 Influence of phosphorus

Ductility curves for alloys doped with phosphorus are shown in figures 4 et 5, respectively for the Fe-13%Cr martensitic et ferritic alloys.

It is seen that at a strain rate of  $2.10^{-3} s^{-1}$ , the decrease in ductility is small, since the coefficient Z is about 85% for both alloys. The maximum decrease is observed at temperatures of 900°C and 1000°C for both alloys.

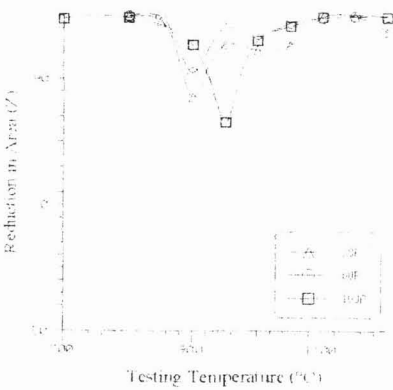
As in the case of alloys doped with sulphur, above about 30ppm, the phosphorus content does not seem to influence the decrease of ductility. However, it does shift the minimum to higher temperature if phosphorus content is increased to 100ppm (about 50°C)

At lower rates ( $2.10^{-4} s^{-1}$ ), the decrease of ductility is larger, and embrittlement does not vary much between 900°C et 1000°C, since the mean coefficient Z is almost constant.

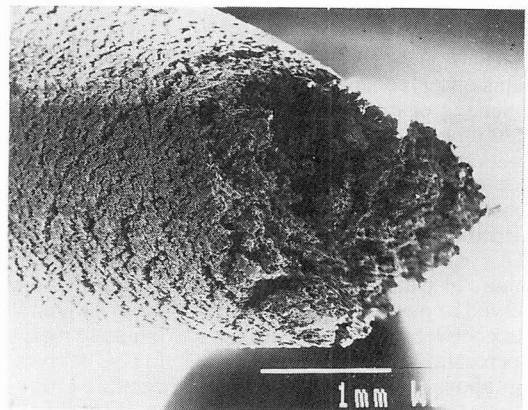


**Figure 4:** Evolution of area reduction at rupture phosphorus doped alloys  
 (a)  $\epsilon = 2.10^{-3} s^{-1}$  (b)  $\epsilon = 2.10^{-4} s^{-1}$

Observed deformed samples of Fe-13Cr-0.2C alloy doped with 100 ppm of phosphorus, show that cracks are not localized in the necking domain, but are spread along the whole sample, as it is seen in figure 6. This type of embrittlement can be evaluated by a factor  $A_f$  or the ratio of cracked surfaces to the surface near the fracture domain. Its evolution with temperature shown in figure 4 for alloys doped with 100ppm of phosphorus, gives a higher factor at a temperature of 900°C, and might indicate a higher embrittlement at this temperature. However, the coefficient Z does not show any evolution, since it is local in character.



**Figure 5:** Evolution of area reduction at rupture 0.02C alloys doped with phosphorus  
 $\epsilon = 2.10^{-3} s^{-1}$



**Figure 6:** Sample of Fe-13Cr-0.2C-100ppmP alloy deformed show that cracks are spread along the whole sample  
 $T = 1050^\circ C, \epsilon = 2.10^{-4} s^{-1}$

#### 4. CONCLUSIONS

Hot ductility curves of Fe-13%Cr alloys doped with sulphur or phosphorus do not show large troughs in the temperature range between 700°C and 1200°C. The segregated elements (S or P) do not seem to play a significant role in ductility reduction.

Observed troughs for deformed alloys doped with sulphur (above 30ppm), are almost the same, being more extended (from 900 to 1100°C) for Fe-13%Cr-0.2C martensitic alloy, as opposed to 0.02C ferritic steel. This large domain of embrittlement is also observed for the deformed 0.2%C martensitic alloy doped with phosphorus, at strain rate of  $\dot{\epsilon} = 2 \cdot 10^{-4} \text{ s}^{-1}$ .

Revealed cracks on the deformed samples show that the fracture mode changes when the sulphur content increases. Fractures are transgranular for low a sulphur content (30ppm S), although they are intergranular for higher levels (100ppm S).

At low sulphur levels, the cohesion of ferritic or austenitic grain boundaries is relatively high. But this effect is reversed at high temperatures, where grain boundary deterioration is stronger.

For deformed Fe-13%Cr stainless steel doped with phosphorus at low strain rates ( $2 \cdot 10^{-4} \text{ s}^{-1}$ ), the ductility trough is deeper and extends over a wide temperature range. However, the embrittlement is not localized. The coefficient Z although necessary, is not sufficient to describe this behaviour. An approach by an evaluation of surface cracks from image treatments seems to give interesting results.

#### References

- [1] Vodopivec F., *Met. Technol.*, 5, 1978, 115
- [2] Erasmus L.A., *J. Iron Steel Inst.*, 32, 1964, p202
- [3] Pichard C. *Thèse de Doctorat d'Etat, Paris VI*, 1976
- [4] Maehara. Y., Ohmori. Y., *Mater. Sc. Eng.*, 62, 1984, 109-119
- [5] Heritier P., Fourdeux A., Kobylanski A., *Script. Met.*, 15, 1981, 995-1004
- [6] Yasumoto K, Maehara. Y, Ura S., Ohmori. Y., *Mater. Sci. Technol.*, 1, 1985, 111
- [7] Tacikowski M., Osinkolu G.A., Kobylanski A., *Acta Met.*, 36, 1988, 995-1004.
- [8] Hipsley C.A., Druce C.G., *Acta Met.*, 31, 11, 1983, 1861
- [9] Yi P. *Thèse de Doctorat, ENSM Saint Etienne*, 1989.
- [10] Mc Lean D., *Grain Boundary in Metals*, Clarendon Press, Oxford, 1957.