CREEP BEHAVIOUR AND STRUCTURAL CHANGES OF Cr2.25Mo1 STEEL AFTER LONG-TERM SERVICE IN HYDROGEN

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Creep properties and structural changes of the Cr2.25Mo1 steel from a pipeline system exposed to 135000 service hours at 530°C with hydrogen at 3.5 MPa as the operating medium were evaluated. No effect of hydrogen on creep properties degradation of the Cr2.25Mo1 steel was detected after this exposition.

However, additional annealing of the exposed material in hydrogen at pressures 5 and 20 MPa at 600°C for 500 and 1000 hours proved significant effect of the annealing pressure and time on creep propeties. Time to fracture and creep rate are determined by the density of fine precipitates inside grains and fracture occurred by the transcrystalline damage mechanism.

INTRODUCTION

Long-term exposure to hydrogen at elevated temperatures may cause degradation of material properties and reduction of service life. Therefore, creep properties and structural changes of the Cr2.25Mo1 steel from a piping system exposed to 135000 service hours at 530°C with hydrogen at the pressure 3.5 MPa as the service medium were evaluated.

EFFECT OF LONG-TERM SERVICE EXPLOITATION IN HYDROGEN

The material for the creep tests was taken from a location exposed in service to stress due to internal pressure only. Besides tests of samples of steel which had been exposed to the service load, tests of unexploited steel were made. The creep tests were made at temperatures 500 - 600°C and the longest tests took 30000 hours. In addition to creep strength also creep curves were obtained in the tests. The basic mechanical properties and the chemical composition of the tested materials are presented in the report by Bína and Hnilica (1).

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Material behaviour under creep

The experimental results were estimated using a complex model of the creep capable to describe the creep curves in all three stages of the creep process. The basic constitutive equation of the model is given by Equations (1) (Bína and Hakl (2)).

$$\varepsilon_c(t|\sigma,T) = \varepsilon_0\left[\frac{\varepsilon_m}{\varepsilon_0}\right]^{g(\pi)/g(1)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where $g(\pi) = \pi^N\left[1+\exp\left(-2\pi^K\right)\right]^M$, $\pi = \frac{t}{t_r}$

t_r time to rupture:

$$\log t_r = A_1 + A_2\log\left|\frac{1}{T}-\frac{1}{A_5}\right| + A_3\log\left|\frac{1}{T}-\frac{1}{A_5}\right|.\log\left[\sinh\left(A_6\sigma.T\right)\right]$$

$$+A_4\log\left[\sinh\left(A_6\sigma.T\right)\right] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The material constants of the constitution equations of the tested materials are published by Bina and Hnilica (1). Only creep strengths and creep rates obtained will be compared. As it can be seen from Table 1, creep strength was found to be lower for the exploited material. A comparison of the minimum creep rates of the exploited and unexploited materials is presented on Fig. 1.

TABLE 1- Comparison of creep strength of the tested materials

Temperature [°C]	Time to rupture [hrs]	Unexploited material creep strength [MPa]	Exploited material creep strength [MPa]	Ratio [-]
525	30 000	123.1	128.8	1.04
	100 000	97.6	91.6	0.93
550	30 000	90.2	88.9	0.98
	100 000	69.1	63.9	0.92
575	30 000	64.8	61.8	0.95
	100 000	48.3	46.0	0.95

The differences seem to indicate the existence of a certain degree of material damage and service life exploitation. However, rather than being due to the effect of hydrogen, the damage can be more or less accounted for by the past operating history of exposure to the service temperature and pressure. These conclusions have been confirmed also by the metallographic analysis.

Metallographic and fractographic analysis

The structure of the exploited material is ferritic-bainitic (about 40% of bainite) - see Figure 2a. Larger particles and the fine needle-shaped precipitates existing inside the bainitic area were found to be M_7C_3 and M_3C carbides and Mo_2C carbides respectively. These precipitates are found mainly inside the ferrite grains. No traces of grain damage due to hydrogen effects were found by the metallographic analysis. Creep exposition at 575°C under 80-120 MPa has induced remarkable changes in the material structure. Bainite gradually dissolves and after 2826 hours no bainite can be detected optically. Important changes also occur in ferritic grains. The needle- shaped M_2C precipitates dissolve and their occurrence is rather rare after 5275 hours (Fig. 2b). Instead, there are three typical carbide morphologies that are typical for this structural pattern. By means of electron diffraction, these carbides were identified to be $M_{23}C_6$, M_7C_6 and M_6C. At 525 °C the structure was studied only up to 3000 hours of exposition and no major changes were observed. In all cases, fracture was transcrystalline and ductile (dimple morphology). Two dimple types were found to exist in the fracture surface: large dimples of about 5 microns in diameter and small ones, most of which were about 1/10 of a micron in diameter.

EFFECT OF PRESSURE AND ANNEALING TIME

Exploited material annealed in hydrogen at 600°C for 1000 hours at pressures 5 and 20 MPa and for 500 hours at 20 MPa and at 530°C for 500 hours at 25 MPa was used to evaluate the effect of hydrogen exposition, annealing time and pressure on creep properties. The same material annealed in air at 600°C for 1000 hours was used as reference material.

Creep strength and strain properties

The creep strength tests data were evaluated using Equation (2). Already at exposition of the material at 5 MPa a 12% reduction of creep strength was observed. With growing hydrogen pressure the creep strength can be seen to deteriorate - see Table 2 - data sets No. 2 and 4. As far as concerning exposition in hydrogen, relatively the steepest decline can be seen to occur already at the very start of exposition - data sets No.3 and 4 in Table 2. Apparently, the degradation of creep strength can be quantified through the A_6 parameter in Equation (2) with all the remaining parameters (A_1-A_5) staying the same for all the studied data sets No. 1-4.

TABLE 2- Effect of annealing in hydrogen on creep strength

No.	Material (data set)	Decrease %)*
1	annealing in air 600°C/1000 hours - reference material	-
2	annealing in hydrogen 600°C/1000 hours, 5 MPa	12
3	annealing in hydrogen 600°C/500 hours, 20 MPa	27
4	annealing in hydrogen 600°C/1000 hours, 20 MPa	34

*) Creep strength reduction compared to material after annealing in air

The effect of hydrogen and time of exposition for creep curves is documented in Figure 3. Creep curves were estimated using relations (1). The shape of strain characteristics can be seen to change in the tertiary stage less distinct with longer annealing times. No major degradation of the plastic creep properties at fracture (ductility and reduction of area) was observed and the characteristics are comparable with those of the original material after exploitation.

Metallographic and fractographic analysis

Long-term annealing of the material in air at 600°C (1000 hours) results in overall homogenisation of the material structure. The original ferritic-bainitic structure is replaced by a ferritic structure containing coarse particles along the grain boundaries and very fine precipitated particles inside the grains. A similar change of structure can be observed in materials exposed to hydrogen with one major difference : the precipitation of fine particles inside the grains is suppressed by the effect of hydrogen. After exposition 600°C/1000 hours at 20 MPa, fine particles are virtually absent (Figure 4a). For all specimens exposed to creep fracture occurred by the ductile transcrystalline rupture mechanism with dimple morphology. Major contraction was observed to occur during the last stage preceding fracture. The fracture surface morphology of the material free of hydrogen exposure was found to comprise a mixture of large dimples interspersed with frequent dimples of diameter smaller by one order of magnitude. In material exposed to hydrogen the character of the fracture surface differs. The number of small dimples is lower. In material after exposure in hydrogen at 600°C/1000 hours, 20 MPa, the fracture surface comprises mainly large dimples which are fairly deep and major plastic strain has occurred during the voids coalescence (initiated at the coarse particles) - see Figure 4b. With transcrystalline damage mechanism, the time to fracture is determined by dislocation creep, i.e. by plastic strain inside the grains (Hancock (3), Cocks and Ashby (4)). The movement of dislocations is arrested the most in a material containing the highest density of the fine precipitated particles. On the contrary, if these particles are absent, the dislocation movement is the easiest and time to fracture the shortest.

CONCLUSIONS

1. No effect of service exploitation in hydrogen for 135000 hours at temperature 530°C and pressure 3.5 MPa on deterioration of creep properties of Cr2.25Mo1 steel was demonstrated to exist by the creep tests performed. No traces of structural damage due to the effect of hydrogen was found to exist by the metallographic analysis. The existing differences in creep behaviour can be accounted for by the normal material exposure at the service temperature and pressure. The creep rate and time to fracture were determined under the given conditions using the power creep law.

2. Annealing in hydrogen atmosphere at 600°C/500 and 1000 hours and pressures 5 and 20 MPa proved a major effect of pressure and annealing time on degradation taking place at the first stages of temperature exposition - see Table 2. The effect of annealing at temperature 530°C/500 hours and 25 MPa was not found to be significant. Time to fracture and creep rate depended on the density of fine precipitates inside the grains and the fracture occurred by the transcrystalline damage mechanism.

SYMBOLS USED

ε_C = total creep strain (%)

ε_m = limit creep strain (%)

t_r = time to rupture (hours)

σ = stress (MPa)

N, M, K = material constants (-)

ε_0 = instantaneous strain (%)

t = time (hours)

π = creep damage (-)

T = temperature (K)

A_1 - A_6 = material constants

REFERENCES

(1) Bína,V. and Hnilica, F., "Žáropevné vlastnosti a strukturní stav provozně exponovaného materiálu potrubního systému Reforming II", SVUM Praha, Report No. 73.6.0234, 1993.

(2) Bína,V. and Hakl, J.,"Probabilistic Approach to Description of the Creep Strain Characteristic and Prediction for Long Life-time", Proc. of the C.R.M. Conference on "Materials for Advanced Power Engineering 1994" Liege, Belgium, 1994., Edited by Coutsouradis, D., KLUWER Academic Publisher.

(3) Hancock, J.W., Metal Science, Vol. 10, 1976, pp. 319-326.

(4) Cocks, A.C.F. and Ashby, M.F., Progress in Material Science, Vol. 27, 1982, pp. 189-197.

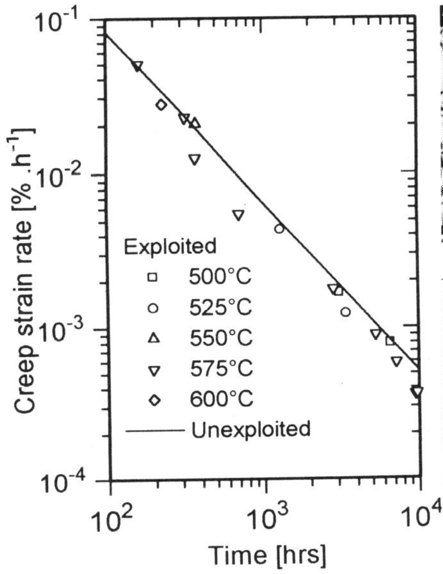
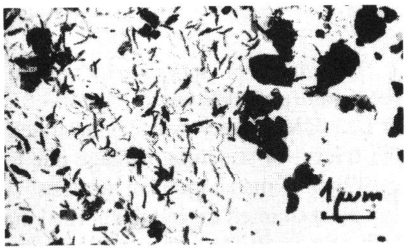
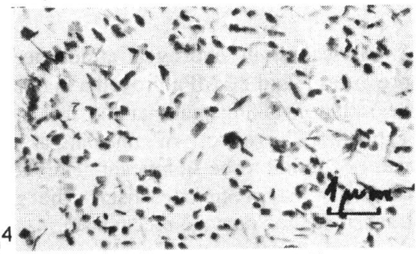


Figure 1 Minimum creep rates of the exploited and unexploited material



a) Transmission Electron Microscopy



b) Transmission Electron Microscopy

Figure 2 a) Exploited material
b) The same material after creep test

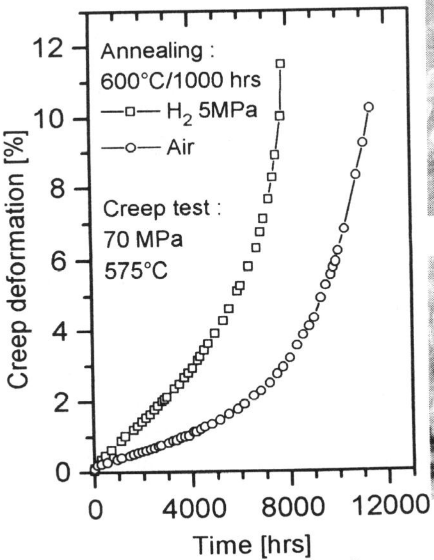
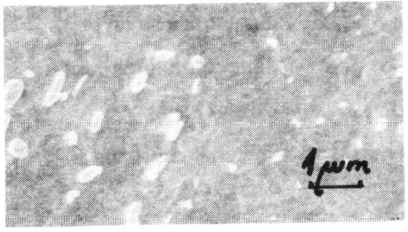
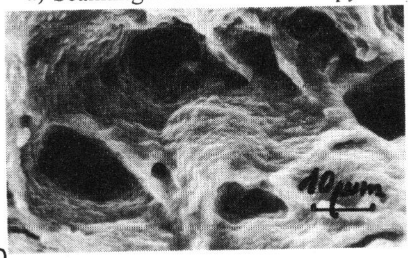


Figure 3 Creep curves after annealing in air and hydrogen



a) Scanning Electron Microscopy



b) Scanning Electron Microscopy

Figure 4 a) After hydrogen exposition
b) Transcrystalline fracture morfology