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DEGRADATION PROCESSES IN CREEP-RESISTING STEELS

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ABSTRACT
This paper deals with processes occurring in creep-resisting steels during long-term degradation at high temperatures. The mechanical and creep behaviour of these materials is compared to their microstructure. The experimental methods, including mechanical testing, creep tests, and structure measurement - light metallography, SEM/TEM, electron and X-ray diffraction, were used.
Keywords: degradation, microstructure, creep-resisting steel

1. INTRODUCTION
The power industry in the Czech Republic must face to getting a lot of power plants on fossil fuels out of use following by incoming necessary modernisation of these power plants. Furthermore, the European trends of energy production even more require a renovation of old power plants or building new ones with super-critical parameters (pressure higher than 30 MPa at temperature of media up 600 °C). The research of degradation processes in materials used in power plants plays very important role for a successful renovation of old plants and for reliable prediction of service lifetime of the new plants. Therefore, the aim of our work was to obtain enough information about creep-resisting steels to be used as materials for super-critical power plants and the processes occurring during the degradation in them.

2. EXPERIMENTAL MATERIAL
In term of the study of degradation processes at high temperature, the creep-resisting steels were used. According to their chemical composition and properties, these steels were divided into four groups:

- creep-resisting carbon steels
- low-alloyed Cr-Mo and Cr-Mo-V-W steels
- martensitic and ferritic Cr steels
- austenitic Cr-Ni and Cr-Ni-Mo steels

Steels of the first group are supposed to be used up to a service temperature of 450 °C at a low loading. In opposite, steels of the second and third groups are supposed to be used up to a service temperature of 575 °C and these are very often used in a power and petrochemical industry. The last group contains high-alloyed steels operating up to a service temperature of 625 °C keeping a high level of corrosion resistance. But, the strength properties together with the cost are their big disadvantages.

The creep-resisting steels were studied after their initial heat treatment and during long-term degradation under service or laboratory conditions.

3. DEGRADATION PROCESSES

The long-term exploitation of a material at a high temperature leads to the structure changes, which influence the mechanical properties and resistance to damage mechanisms as well [1]. To describe various processes, the tests of mechanical properties, structure measurements, creep and corrosion tests were carried out. The results are mentioned in following text.

3.1. Creep

The creep tests with isothermal (450 °C, 500 °C, 550 °C, and 600 °C) and cyclic temperature loading on experimental materials at state after initial heat treatment and after long-term degradation annealing as well were carried out. The tests brought following results (also in Figure 1).

High-alloyed Cr steels have a high level of creep resistance and the degradation annealing 650 C/10 000 hours (under laboratory conditions) leaded to only low decrease in this creep resistance. Despite, the effect of cyclic loading was opposite. The values of the time to fracture of all these Cr steels were higher. But creep behaviour of steel N10 (low-alloyed Cr-Mo-V-W steel) was different. This steel at the state after long-term service (450-500 °C/200 000 hours) had higher creep lifetime than after the initial heat treatment. This fact was effected by precipitation of very fine carbides in the matrix of the steel during the creep test. On the other hand, this precipitation had negative influence on elasto-plastic behaviour, especially on creep rupture elongation (decreased on a half). In opposite, steel T23 (low-alloyed Cr-Mo-V-W steel too) had a good creep resistance at the state after initial heat treatment, but the isothermal long-term annealing (in laboratory) induced the decrease in a creep lifetime about 2 orders. This degradation of creep resistance was effected by coarsening of the primaly precipitated carbides on the grain boundaries. Furthermore, the cyclic loading had no effect on the creep behaviour of this steel.

3.2. Corrosion

All materials operating in oxidation ambient must face to the corrosion. Creep-resisting steels are usually alloyed with chromium and nickel, i.e. elements increasing corrosion resistance. Anyway, these steels underlie the oxidation during the long-term annealing and oxides on surfaces occur. The thickness of oxide layer depends on the annealing time and temperature. There are many models of oxidation growth and methods how the oxidation should be measured. We observed the thickness of the oxidation layer on the surface of each studied materials (see Figure 2) and compared achieved data. As the result, we divided the creep-resisting steels according to the corrosion resistance. The order of the steels in the corrosion resistance line is given by the amount of chromium and nickel in the matrix of steels. The most corrosion resisting steels are those with an austenitic microstructure, the less resisting steels are carbon and low-alloyed Cr-Mo-V-W steels. Moreover, because the oxidation was accompanied by decarburisation, so, the decarburisation was observed too [2].

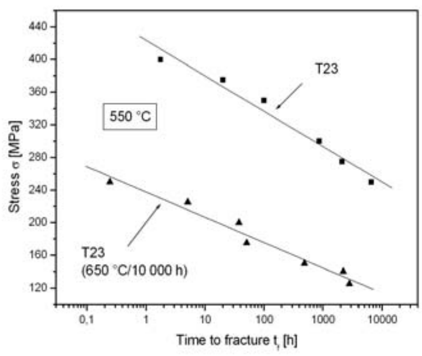

Figure 1. Dependence of creep stress on time to fracture

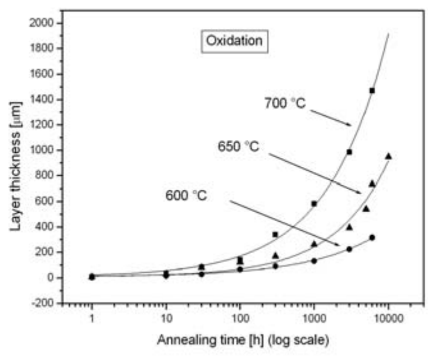

Figure 2. Dependence of oxidation on annealing time

3.3. Embrittlement

The hydrogen and temper embrittlement was observed in creep-resisting steel IN9 after service degradation at the temperature 300 °C for about 140 000 hours in a hydrogen ambient (the initial state of the steel IN9 was achieved by regeneration annealing 610 °C/2 hours followed by the quenching into water [3]). A level of the embrittlement was evaluated in consideration of Charpy tests at various test temperatures and in accordance to the metallographic measurement.

A long-term operation of petrochemical plants in hydrogen ambient induces the embrittlement of the materials (3 Cr-Mo-W-V type of steels) the plants are made of. The mechanism of the degradation is controlled by complex hydrogen effect, creep at service temperature above 400 °C, and temper embrittlement mechanism at temperatures between approx. 325 and 450 °C.

The temper embrittlement was induced by impurities (phosphorus, tin, eventually antimony, arsenic) in the steel and their segregation on the grain boundaries. As a result of the embrittlement, the steel was damaged by inter-crystalline fracture and the transition temperature of the notch toughness increased about approx. 70 °C. Simultaneously, the hydrogen assisted embrittlement occurred. The free hydrogen penetrated into the matrix of the materials and reacted with phosphorus on the grain boundaries. So, the captured hydrogen decreased in the cohesion of prime austenitic grains and caused the fragile behaviour of the steel. Fortunately, the embrittlement was reversible and could be cured by isothermal annealing above 600 °C followed by quenching.

3.4. Degradation of microstructure

Due to the high temperature, the structure changes are usually controlled and accelerated by diffusion mechanism occurring in the whole volume of the material [4]. The diffusion enables the movement of carbon and other elements to create carbides particles. These carbides particles have a various morphology, location and chemical composition. According to all these properties, carbides particles increase or decrease the creep-resistance and influence the behaviour of the steel. Analysing the results, carbon steels (group 1) inclined to corrosion and decarburisation. The steels with ferritic-bainitic microstructure changed the microstructure during the degradation. The coarsening of precipitated particles on grain boundaries decreased the creep-resisting behaviour, but the precipitation of new very fine carbides operated in opposite. Furthermore, the precipitation of brittle inter-metallic phases as Laves or Z-phases occurred in high-alloyed steels with martensitic microstructure during long-term annealing at temperature about 625 °C.

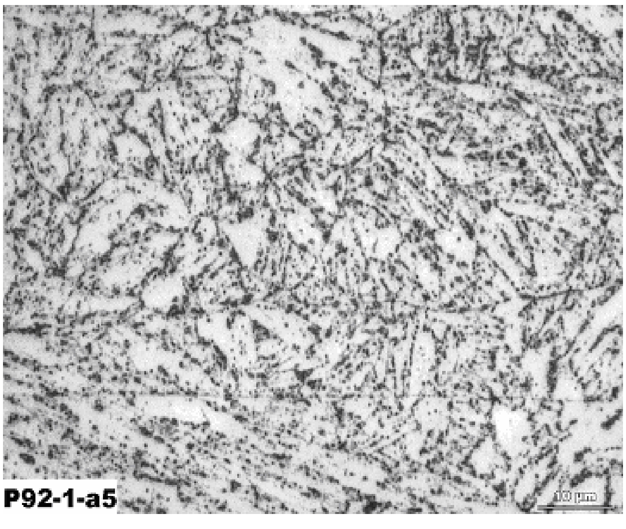

Figure 3. Microstructure of 9% chromium steel after initial heat treatment (light microscopy)

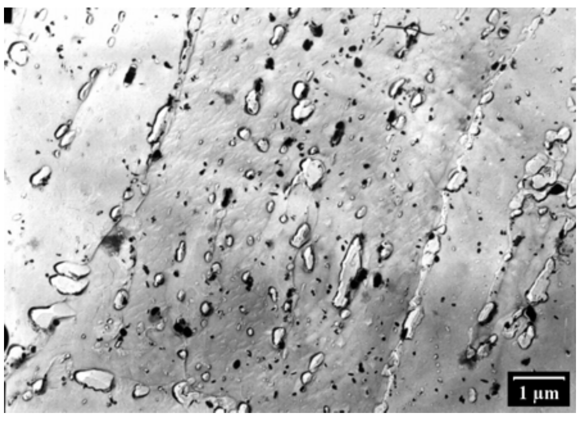

Figure 4. Morphology of carbides particles in 9% chromium steel after long-term annealing (electron microscopy TEM)

3.5. Degradation of mechanical properties

Changes of mechanical properties are tightly bound to microstructure changes. During the degradation, the inter-particle distance grows and the hardness of the material decreases. Opposite, the precipitation of fine particles causes the increase of hardness and strength behaviour. The dependence of hardness on inter-particle distance and strength values on Larson- Miller's parameter (time – temperature dependence) is shown in figures 5 and 6.

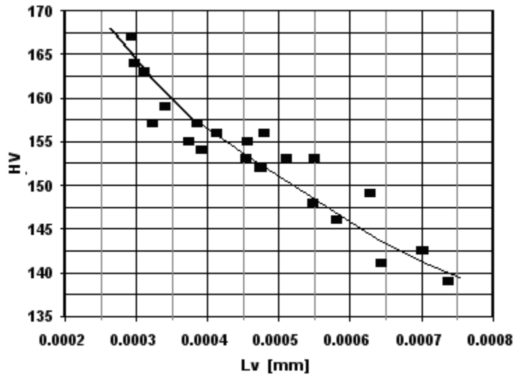

Figure 5. Dependence of hardeness on interparticle distance L_V

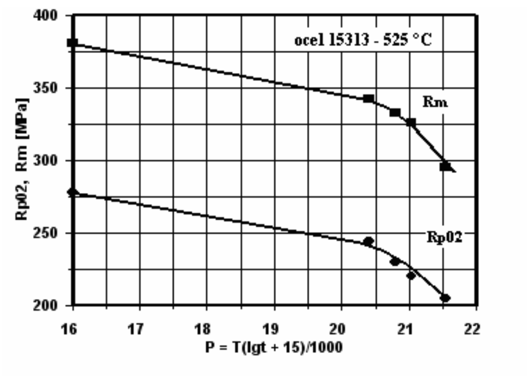

Figure 6. Dependence of strength values on Larson-Miller's parameter

Of course, the degradation is not a task of only one process and mechanism, but of the combination of all possible processes and mechanisms. Thus, to get a real description of degradation process in any material, it is necessary to take all possible mechanisms and processes in account.

5. CONCLUSION

Our research was focused on study of degradation processes occurring in creep-resisting steels during long-term exploitation at high temperatures. The experimental materials were studied after the initial heat treatment and during the long-term degradation annealing as well. The achieved values of mechanical properties and creep behaviour of these materials were compared to the changes of their microstructures. The experimental methods, including mechanical testing, creep tests, and structure measurement - light metallography, SEM/TEM, electron and X-ray diffraction, were used. According to the results, the creep-resisting steels can be compared with each other and the achieved values of mechanical, creep and corrosion properties can be used as input data for service lifetime calculations.

6. ACKNOWLEDGEMENT

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