DEGRADATION OF CZECHOSLOVAK CREEP RESISTANT STEELS AFTER 50 YEARS OF SERVICE

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Resume

Thermally loaded assemblies in the energy and chemical industries require materials that provide the necessary functional characteristics, even after very long periods of operation. For the assessment of these materials are used expression grade of degradation in the basic meaning of the original English word grade = quality grade, where the degradation is cumulative deterioration of quality (properties) and thereby reduce the utility value. Knowledge of these mechanisms acting simultaneously allows determining the boundary conditions and more efficient utilization of used materials. Alternatively, it may give information to a qualified estimate of the causes of failure. Degradation starts its own production of semi-finished products (purity, structural homogeneity) continues through technological factors of production (welding) and the last part of degradation is during service of the parts (corrosion, hydrogen embrittlement, etc.).

The aim of this article is at bases information obtained from fifty years of degraded materials to obtain information for more accurate reference catalogue. This catalogue can on bases information obtained from the microstructure and hardness estimate the state of degradation or possible time to rupture for the material.

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1. Introduction

Already in the sixties, an achieving a lifetime of 2 to 2.5 x 10^5 operating hours was usual requirement for basic parts of power equipment and parts with difficulty changeable, especially boilers for production of steam. The main part of technology of Czechoslovak power plants, but also all other boilers manufactured till 1985, was made from domestic (ČSN) steels. When boilers K4 and K5 in power plant Hodonín were cancelling it managed to get operationally exposed sample of the original used creep resistant steels. These samples can be compared with samples taken from other boilers, but also evaluation of degradation materials used in UJP PRAHA a.s.

Apart from sophisticated methods of controlled ageing, which are used for large power plants boilers, where the high cost of gathering, archiving and evaluating of data is economically worthwhile, also several thousands of small units in the Czech Republic are still in operation. Economic conditions and large diversification of operators of medium and small boilers using fossil fuels, comparatively frequent change of owners and operators are strongly reflected in the continuity of transmission of information about traffic, faults, structural interventions and technology interventions. In recent years, there is increasing number of cases when operators make experiments with different fuels without significant knowledge of initial state of the device. Many boilers are on the edge of survival and often significantly behind. Nevertheless, the operators must take guarantees (especially for heating plants) for continuity of energy supply to customers. Possibility to assess this device using probabilistic lifetime analysis methodology and risk of failure of boilers, which is developed by major operators of boilers (especially electrical) in complex controlled ageing programs, is for these small devices unrealistic. Reasons are quite simple, there is a **lack of input data**, documents about operation and high financial demands on this comprehensive solution. Therefore, information about the long-term behaviour of exposed steel is very valuable.

2. Selection of suitable steel

A wide range of steels has been used for the construction of these devices. First, it was the steel at the most exposed part of the device, which was devoted to critical attention (especially on ČSN steel grades 15 and 17), and the other parts that were primarily made of steel grade 11, 12 and 13. Specifically, it is supposed to be some ČSN steel 11 354, 11 366, 11 416, 11 474, 12 021, 12 022, 12 025 and 13 123, or their foreign equivalents produced and trade within the CMEA (the Council for Mutual Economic Assistance).

While the exposed parts of boilers were during years of operation one or more times replaced, the other parts are very often the original ones. That means they were under very long-time operation influenced by different degradation mechanisms. These long-time exposed parts are usually made from ČSN steel 12 022 for evaporator pipes and other transit areas, and from ČSN steel 13 123 used for thick-walled components (i.e. chambers and boiler drums).

2.1 Ageing of carbon steel

Temporal change in physical and mechanical properties of alloys, on which intensity and speed temperature has decisive influence, is known as ageing [1]. It is a token of “effort” of material to reach steady state, i.e. attempts to remove the non-equilibrium state induced by the last processing. That is characteristic of the phenomenon of ageing, described already in 1936 by Epstein and Miller [2] to describe changes in the properties of steel. Generally, the ageing is characterised by the separation of secondary phases in the decay of an unstable supersaturated solid solution of the base material, therefore by the process of precipitation. In addition to precipitation, the structurally multi-component alloys subject to changes in structural components primarily excluded during thermal ageing too, considering steel already in the decay of austenite or pearlite, respectively bainite in case of creep resistant carbon steel. It means that ageing presents in creep resistant weldable low carbon steel used up to temperature of approximately 400 °C for the construction of energy and chemical facilities.

One of the fundamental properties of low carbon steel for power industry is a guaranteed, respectively conditional guaranteed weldability. Of course, the installers should follow instructions against the negative influence of hydrogen on the quality of welds. But as stated in [3] by Hrivňák, there are not rare complications with ageing of weld, where the risk of ageing addition is attributed not only to carbon, but to the nitrogen content too. Nitrogen content can reach 0.007 wt. % in martensitic steel. Ageing may occur especially in a heat affected zone (HAZ). This ageing of weld exhibits by excluding iron nitrate and sharp decline in toughness [4, 5].

Carbon creep resistant steel has ideally structure formed by lamellar or globular pearlite or upper bainite or mixtures of thereof. Lamellar pearlite is not in terms of structural stability fully equilibrium structure. Exposure to sufficiently high temperature can induce lamella surface collapse into a spherical shape [6]. When the operating conditions are optimal, the collapse process is slow and long-term and lamellar colonies of pearlite make globular shape slowly. This phenomenon is accompanied by decreasing of hardness [7]. Next part of the change is coagulation. Fine cementite globules are growing and distance between them are growing too. This phenomenon is accompanied by a further decrease of strength properties and sharp decreasing of hardness. At the same moment, structural phases are excluded from solid solution of ferrite followed by their coagulation. It leads to gradual loss of interface between pearlitic formations and ferrite, and to considerable variance in decay products. Steel which passed through this degradation process is usually in terms of mechanical properties already below the lower limits of strength values. Structural components of bainite are again ferritic and cementitic, but unlike the pearlite in fine ferrite-cementite dispersion without significant interaction between the two components. Lower temperature of transformation of austenite is reason for a lower diffusion rate of carbon and for self diffusion. In case of carbon creep resistant steel a possible microstructure is upper bainite that closely resembles pearlite by its morphology. Degradation of mechanical properties during ageing is structurally characterised by growing cementite parts, growing distance between particles and loss of interface between ferrite and bainitic components.

2.2 Mechanical damage of carbon steel

Many times repeated analyses showed that the lifetime of pipes and chambers of heat transfer system is affected by these basic degradation processes [8], which mainly act simultaneously:

- loss of wall thickness due to mechanical damage (which is mostly local abrasion),
- surface damage due to the outer surface corrosion,
- surface damage due to the inner surface corrosion,
- changes in surface structure of the material due to the effect of diffusion processes,
- changes in structure caused by the long-term effects of high temperature,
- initiation of irreversible defects caused by external tension,
- effect of weld joints and their different behaviour under long-term operational stress loading.

The life of the chambers and boilers is not usually limited by the thickness decrease due to mechanical corrosion, but the initiation and propagation of cracks and changes in geometry caused by long-term effect of temperature in combination with stress. The most probability of defects presence is in HAZ of weld joints.

2.3 Two areas of damage mechanisms

The evaluation of materials damage is complicated somewhat by the fact that steel with guaranteed carbon content is used in boilers in a relatively wide range of operating temperatures, often very different from the project values. It is necessary to determine a relevant temperature level where creep process starts to be applied. Because there is not a sharp boundary and many applications vary precisely in this temperature level it is often a subjective decision. However, for the calculation of basic dimensions of pressure equipment working up to creep condition the yield strength is used whereas in creep conditions time depended creep strength is used [9]. These two variables have not same values. Although in general principle is that use of lower values, but the most of historical documents of most devices that operate in this temperature range creep neglect.

Because the computational codes used for the design of historical boilers take as a comparative value ultimate, respectively yield strength, it is possible to use these codes with correct value of strength for new materials. And this method for new material is maintaining full control of the analytical procedure. The advantage of this procedure is the possibility of maintaining the original strength documentation of boiler. And this method is acceptable for controlling organisation.

2.4 Problems with residual life assessment based on structural changes

For assessment of residual life and risk of failure there is an approach recommended in UJP PRAHA a.s. based on structural changes, especially on the degree of globularisation of pearlite. This is procedure that gives very good results in considerable heat-exposed parts such as super-heaters. The procedure was tested not only on samples prepared in experimental laboratory [10], but even on samples of material collected from long-term operating boilers. The only limit that restricts the use of this procedure is that the structural changes in evaluated in-service exposed materials were not only due to operating temperature, but stress loading as well. For parts that are less thermally exposed structural changes can be caused by initial heat treatment which may be misleading for evaluation.

2.5 Method for the determination of service life based on spheroidisation of structure

Effect of thermal exposure occurs in creep resistant carbon steel and low-alloy steel with spheroidisation and extraction of carbides at grain boundaries (later inside the ferrite grains) and their gradual coarsening. For this purpose a table of representative structures for various states of degradation of carbon and ferritic-pearlitic steel was made. The structures are classified into 6 basic degrees with typical morphology for the state. These degrees are in short characterised in the following Table 1.

This approach maps the morphological changes induced by long-term effect of temperature which leads to the gradual deterioration of the mechanical properties of creep resistant steel. For using this approach we assume uniform microstructure degradation, i.e. comparable conditions in the entire system (used materials with the same or very similar virgin properties, the same operational conditions such as pressure and temperature and same corrosion condition, i.e. the same speed of loss thickness of bearing section). Use of this approach to assess the condition of the tubes for heat exchange systems is less accurate because it does not guarantee that the selection of monitored place (sampling points) will always represent the area exposed to the greatest effect of degradation mechanism.

Table 1

Characteristic of degradation phase of structure.

Degree of degradation	Ferritic-pearlitic structure	Ferritic-bainitic structure
A	Pure ferritic grain + pearlite	Pure ferritic grain + bainite
B	Incipient spheroidisation of cementite lamellae in pearlitic grains and isolated precipitation of grain boundary ferrite	Incipient precipitation of carbide on ferritic grain boundary, begin of coarsening of carbide in bainite
C	Significant spheroidisation of cementite in pearlite grains, ongoing precipitation of carbide at grain boundary ferrite	Observable coarsening of carbide in bainite, finishing of precipitation ferrite, coarsening of carbide on grain boundary
D	Nearly complete spheroidisation of cementite, rough carbide on grain boundary, weak precipitation of carbide inside of grain	Rough carbide, deletion of difference between ferritic and bainitic grains
E	Rough sphere carbide inside grain and on grain boundary, participial deletion of difference between ferrite and pearlite grain	Rough globular carbide into grain and on grain boundary, ferrite-carbide morphology
F	Rough carbide mainly on grain boundary, some carbide inside of grain	Rough carbide mainly on grain boundary, some carbide inside of grain

For ČSN steel 12 022 it is possible to assign hardness for six degrees of degradation (compare Table 1):

- Grade A – over 153 HV
- Grade B – from 142 to 175 HV
- Grade C – from 130 to 157 HV
- Grade D – from 122 to 147 HV
- Grade E – from 112 to 138 HV
- Grade F – under 128 HV

According to the measurement results on long-exposed samples relationship between hardness and yield strength and tensile strength were determined and complemented. Mechanical properties were measured by tensile strength tests. These relations allow the direct use where it is necessary to perform rapid approximate evaluation of the state of heat exchange surface.

2.6 Long-exposed ČSN steel 12 022

Samples obtained after long-term operating exposition from steel grade 12 were divided into two groups. First group was tested, the second group was first laboratory aged (i.e. placed in an electric resistance furnace and kept at a temperature of 525 °C for 10,000 hours) and then subjected to the same mechanical tests and inspections as first group. Furnace temperature has to be high enough compared to the usual range of application temperatures (based on Larson-Miller construction) to obtain information on the likely structural changes of material for more than five years of operation at the operating temperature.

The aim of the experimental programme was to verify the model procedures that would allow predicting the degradation processes related to the operating conditions. Replicas from surface of laboratory exposed samples were prepared and evaluated by transmission electron microscopy where dimensions of cementite lamellas (a width and a length) were measured. With higher decay of materials solid solution the ratio of widths (w) to lengths (l) of lamellae of cementite is approaching one.

For a similar mechanism - particle coarsening – a model equation that allows calculating the thermodynamic data of particle size changes depending on the temperature and time of isothermal exposure was derived. Besides coarsening of super-critical dimension particle while dissolving sub-critical dimension particles, changes in the shape of the particles occur during globularisation. This shape change is the dominant diffusion process. In terms of the growing behaviour we consider enlarging thickness for diffusion as growth and reducing their length for diffusion dissolution. Therefore, the growth equation was applied to these processes and it was verified that this application is physically acceptable, i.e. the previous assumption is correct.

Fig. 1 shows an experimentally determined dependence of hardness HV on the ratio w/l. The graph in Fig. 1 includes the limits of tolerance hardness values for probability $p = 0.95$.

Next, results of mechanical properties obtained from tensile strength tests allowed creating a relationship between hardness, yield strength, and tensile strength (see Fig. 2). The graph in Fig. 2 includes the limits for $p = 0.95$ again. At the same time, values and relative proportions of strength properties and hardness were observed. It was found that it is not constant, but the value Rp02/HV and Rm/HV depends on the degree of degradation of the structure.

By plotting of dependence of hardness on globularisation of cementite in pearlite grain (ČSN steel 12 022) obtained after fifty years of operation and subsequent laboratory exposure we get the graph in Fig. 3. The experiment confirmed the expectation that the pressure system operating at low temperatures does not face significant structural changes even after more than fifty years of operation. The experiment is in accordance with the generalised dependence of strength on the structural parameters (see Fig. 3). According to the values measured on the parts of one of the closed pressure system it appears that the resistance of the structure against the structural changes (specifically globularisation of pearlite in ČSN steel 12 022) is not linear and decreases with increasing content of globularised pearlite. This is shown by a change of generalised dependence in Fig. 3.

2.7 Long-exposed ČSN steel 13 123

The same experimental procedure as for samples of ČSN steel 12 022 was used for samples of bainitic ČSN steel 13 123. The observed rate of decline of mechanical properties was similar to ČSN steel 12 022. Decrease in tensile strength and yield strength after fifty years of operation was only the depletion of reserves. This reserve was resulting from the use of virgin material with higher strength values than was required by the standards as a minimum. Drum of boiler during its demolition still fulfils condition of operation by strength calculation, including allowable stress values. In terms of decrease of tensile and yield strength degradation annealing (10^4 hours at 520 °C) had comparable effect as fifty years of operation.

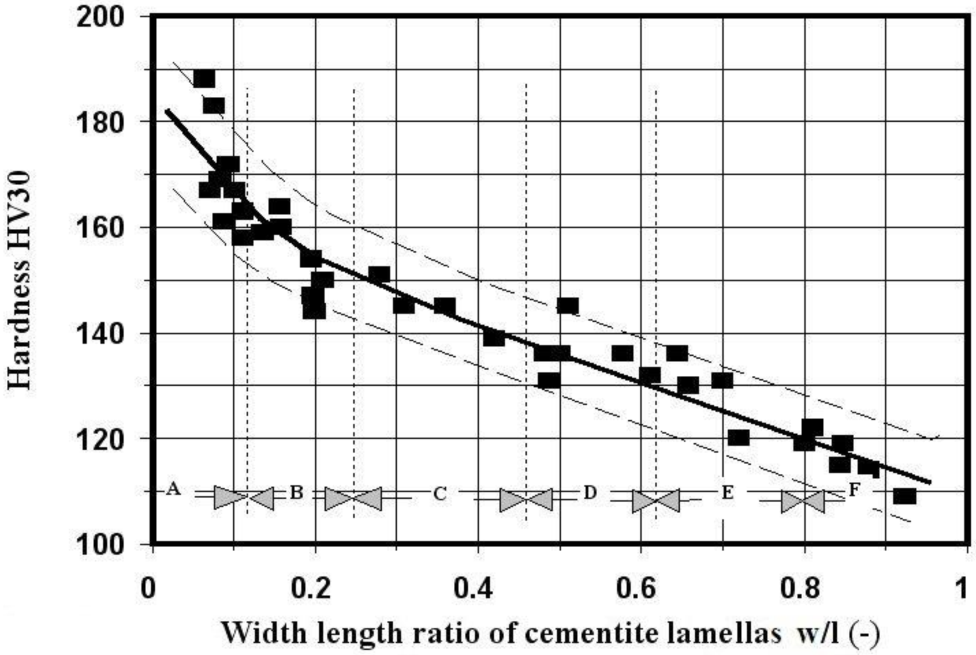

Fig. 1. The dependence of hardness on globularisation of cementite for ČSN steel 12 022.

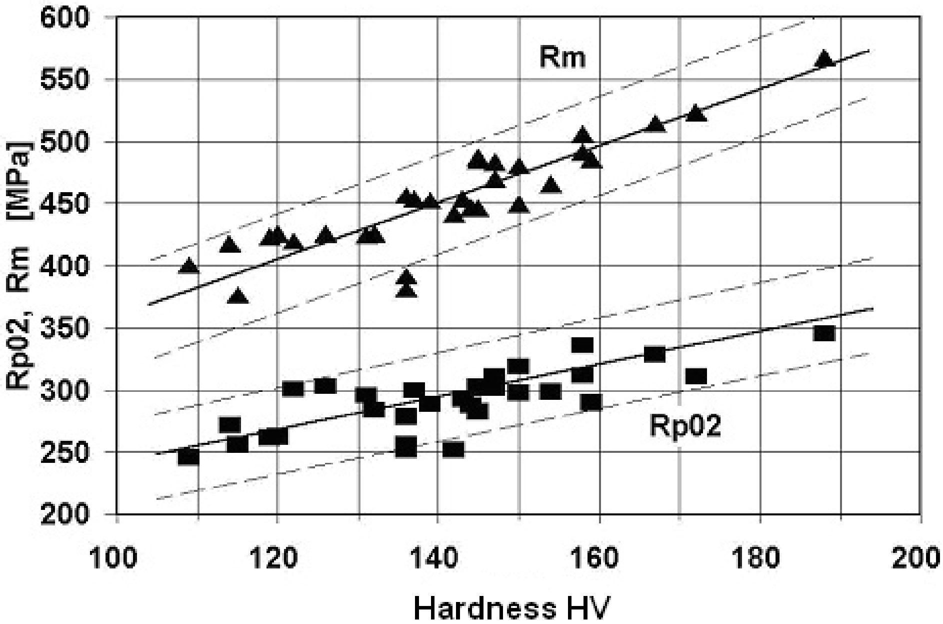

Fig. 2. The dependence of strength on hardness of ČSN steel 12 022.

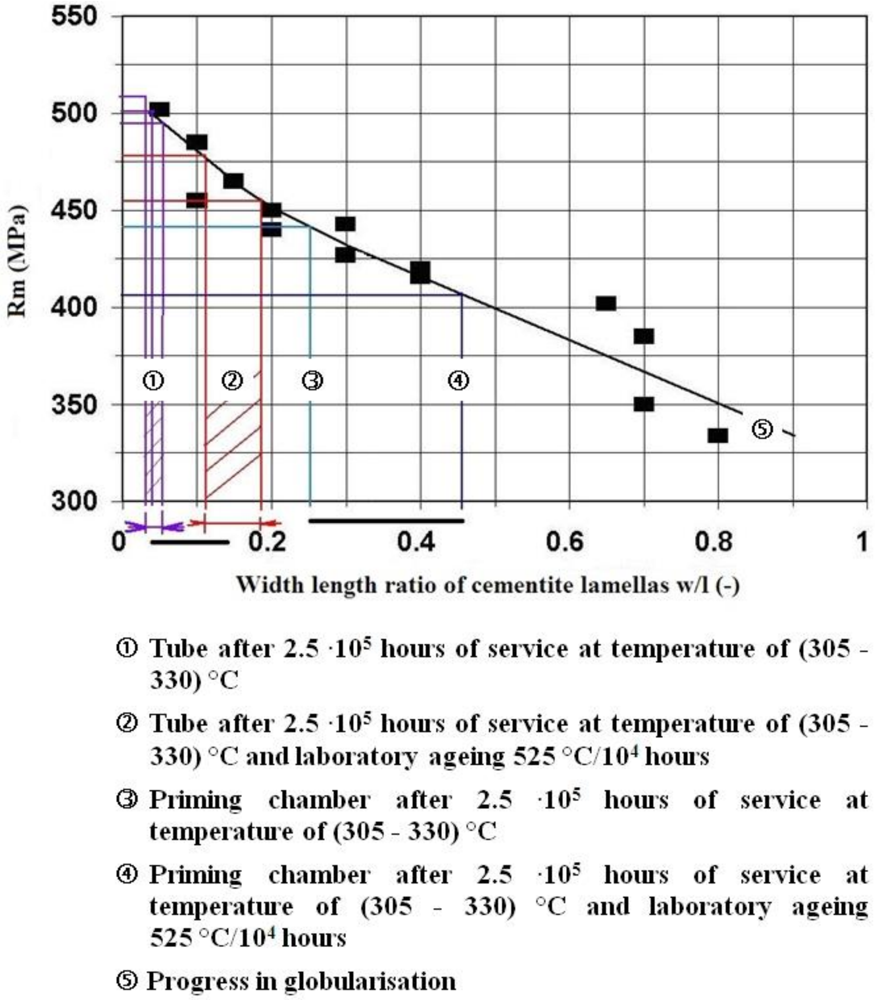

Fig. 3. The dependence of tensile strength on structural parameters.
(full colour version available online)

3. Conclusion

Work performed on long-term exposed samples from ČSN steels 12 022 and 13 123 allows to contribute with new information into UJP PRAHA a.s. continually updated catalogue containing characteristic structural changes obtained using replica sampling. Furthermore, it was confirmed that for these two grades of steel it is possible to make a rough estimation of achieved materials degradation and residual life at the same operational temperature just comparing non-destructive structural images (by replica method) and the catalogue data considering the measured hardness values outside the decarburisation layer.

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