Microstructure changes responsible for the degradation of the 10CrMo9-10 and 13CrMo4-5 steels during long-term operation

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Abstract

The paper presents results of microstructure and mechanical testing examinations performed using optical and transmission electron microscopy, tensile tests and Charpy tests on 10CrMo9-10 and 13CrMo4-5 steels, before and after they were long-term operated at elevated temperatures in a steam heater. In the 10CrMo9-10 steel, the optical microscopy detected a degradation of original bainite that was accompanied by the formation of ferrite, precipitates and micropores. The transmission electron microscopy revealed that the precipitates are M\(_{23}C_6\) and M\(_7C_3\) type carbides, which are located mainly at the boundaries of former austenite grains, and M\(_3C\) type carbides, which appear inside the grains. The 13CrMo4-5 steel contained a relatively high amount of ferrite in the ferritic-bainitic/perlitic microstructure already in the originally state. The degradation of the microstructure was less serious than for the 10CrMo9-10 steel. The thermal treatment of the 13CrMo4-5 steel led mainly to the precipitation of carbides. The M\(_{23}C_6\) and M\(_7C_3\) type carbides form in perlitic-bainitic areas, while M\(_3C\) and M\(_6C\) type carbides precipitate in ferrite. The higher density of the grain boundary precipitates in the long-term operated 10CrMo9-10 steel facilitated the formation of creep-induced micropores and contributed to the hardness reduction.

1. Introduction

Construction steels used in power industry, e.g., 10CrMo9-10 [1, 2], 13CrMo4-5 [3, 4], 16Mo3 [5, 6] or X10CrMoVNb9-1 [7, 8] are required to have specific strength properties like guaranteed yield stress and creep strength both at room and elevated temperatures. These requirements are usually fulfilled in a fresh material, where the appropriate microstructure (ferritic-perlitic, ferritic-bainitic, bainitic, martensitic) is adjusted via normalizing or via quenching and tempering. If the construction steels are subjected to long operation times at elevated temperatures, they undergo microstructure changes, which are accompanied by the deterioration of mechanical properties that can be a very critical issue for industrial safety. It is worth noting that the temperature of the operation is just one factor deciding about the degradation process. Additional factors are the temperature changes induced by the heating and cooling, the loading duration, the stress level and the degree of the surface oxidation, in particular if the steels are used for construction of pipes in a steam heater. The degradation process starts typically with the formation of precipitates and creep micropores (voids), continues with the production of microcracks and ends with the materials destruction. An important basis for the description and explanation of the degradation processes running in these steels is their microstructure examination in certain periods of the operation time [9–15]. For this reason, numerous analytical methods are used that include X-ray diffraction (XRD) analysis [2], optical microscopy (OM) [16, 17], scanning electron microscopy (SEM) [16, 17], atomic force microscopy (AFM) [4, 18, 19] and transmission electron microscopy (TEM) [12, 20]. TEM allows, in particular, a precise determination of the type of precipitates.
2. Materials and experimental methods

The test materials in this study were the 10CrMo9-10 and 13CrMo4-5 steels. Their chemical compositions (table 1) were measured using the spark emission spectroscopy by a Spectrolab spectrometer. The spark emission spectroscopic measurements were carried out on five areas in the central portion of the specimen. During the long-term operation (130,000 h at 480 °C and 23,000 h at 550 °C, respectively, s. table 1), the outer surface of the steam heater coil walls was in contact with the flue gas containing volatile compounds that stem from the low-emission combustion and co-firing of biomass. The inner surface of the pipe wall was in contact with water vapor. The microstructure and microhardness of the worn samples were studied on the cross-sections of the pipe walls.

The microstructure examinations comprised:

1. Microscopic examinations using an optical microscope Olympus GX41 and a transmission electron microscope TEM JEM-2200FS. The observations in optical microscope were performed on polished cross sections of the pipe walls. The TEM investigations were carried out on precipitates that were extracted from the samples.
2. Microhardness measurements using the Vickers method and Shimadzu HMV-G20 microhardness tester. For the microhardness measurement, the same specimens used already for optical microscopy were utilized. Five indentations were made in each area, i.e., in the inner as well as in the outer surface of the pipe wall, and in the middle of the pipe wall cross-section.
3. The static tensile tests at room temperatures using the Zwick Roell Z100 testing machine to determine the tensile strength Rm, and the yield point Re.
4. The Charpy V-notch impact tests.

3. Results

3.1. Steel 10CrMo9-10

In the initial state (figure 1, upper left panel), the 10CrMo9-10 steel possesses a bainitic microstructure. Mechanical properties such as Rm, Re and KV of 10CrMo9-10 steel before operation were 605MPa, 345MPa and 156J respectively. After the long-term operation, the microstructure of the steel consists of a mixture of degraded bainite, small amount of ferrite, precipitated carbides and micropores (figure 1). The bainite areas have an irregular shape along the entire cross-section of the tube wall. The precipitates are concentrated at the boundaries of former austenite grains. Within the grains, the precipitates appear sporadically. Selected area electron diffraction (SAED) in TEM detected three kinds of carbides—cubic M23C6 with the space group Fm3m, orthorhombic M3C with space group Pmn21 and orthorhombic M7C3 space group Pnma. The M23C6 and M7C3 precipitates are located mainly at the grain boundaries, where they form so-called ‘chains’ (figure 2, left-hand panel). The carbides of the type M2C3 appear also within the former austenite grains. Local chemical analysis using EDX analysis in TEM (figure 2, right-hand panel) confirmed the presence of (Cr, Fe, Mo)23C6, (Cr, Mn)23C6, (Mn, Mo)23C6, Cr2C3, (Mn, Fe)23C6, (Fe, Cr)23C6 and (Fe, Mn)23C6. The amount of the carbide precipitates varies across the cross-section of the tube wall. It is higher near the outer side of the wall than at the inner side of the pipe (figure 1). The precipitation of carbides is facilitated by the long-term operation under creep conditions, which additionally promotes the formation of creep micro pores (voids). This process is more pronounced at the outer side of the tube wall, where more micropores appear than on the inner wall side. The lowest concentration of the voids was observed in the central part of the tube (figure 1). However, the process of voids formation is rather moderate in the material under study, as the voids still do not form so-called ‘eights’, which may produce microcracks.

The precipitation of carbides is enabled by the out-diffusion of carbon from bainite that leads to the formation of ferrite grains, which were detected by optical microscopy (figure 1), and to the decrease of the microhardness. Before the thermal treatment, the hardness of the 10CrMo9-10 steel was 251.8 HV0.1. After exploitation, the microhardness decreased. It was the lowest on the outside of the tubes (170.6 HV0.1) and highest in the tube center (figure 3). The trend of the microhardness follows the dependence of the amount of precipitates and the density of the voids on the distance from the tube surface facing the flue gas. During the steel exploitation, the alloying elements diffused out of the matrix and formed, together with carbon, the carbide phases discussed above. The precipitation of carbides led to a change in the chemical composition of the matrix and to a disintegration of the original bainite structure.

The values of tensile strength and yield strength obtained in a static tensile test for the 10CrMo9-10 steel after operation amounted to 522MPa and 305MPa, respectively (table 2). The impact strength for this steel was 112J...
Table 1. Chemical compositions of the examined steels (10CrMo9-10 and 13CrMo4-5) as determined using spark emission spectroscopy and compared with the chemical compositions according to the European norm. Parameters of the high-temperature treatment are given in second part of the table.

| Type of steel | Acc. | Chemical composition, wt% | Parameters of exploitation |
|--------------|------|---------------------------|---------------------------|
|              |      | C   | Si     | Mn      | P       | S       | Cr       | Mo       | Temperature, °C | Time, h |
| 10CrMo9-10   | analysis | 0.12 ± 0.002 | 0.18 ± 0.005 | 0.51 ± 0.007 | 0.009 ± 0.0004 | 0.007 ± 0.0004 | 2.23 ± 0.03 | 1.10 ± 0.004 | 480 | 130,000 |
| 10CrMo9-10   | EN 10028-2 [21] | 0.08-0.14 | max. 0.50 | 0.40-0.80 | max. 0.020 | max. 0.010 | 2.00-2.50 | 0.90-1.10 |
| 13CrMo4-5    | analysis | 0.17 ± 0.002 | 0.31 ± 0.006 | 0.55 ± 0.007 | 0.009 ± 0.0004 | 0.009 ± 0.0005 | 0.86 ± 0.008 | 0.48 ± 0.002 | 550 | 23,000 |
| 13CrMo4-5    | EN 10028-2 [21] | 0.08-0.18 | max. 0.35 | 0.40-1.00 | max. 0.025 | max. 0.010 | 0.70-1.15 | 0.40-0.60 |
Despite the observed changes in the microstructure and mechanical properties, the parameters $R_m$, $R_e$, $K_V$ and $H_V$ of the 10CrMo9-10 steel meet the requirements of the standard [21] even after the operation after 130,000 h at 480°C.

Figure 1. The microstructure of the steel 10CrMo9-10 before and after operation as seen by optical microscopy.

Figure 2. Bright-field TEM (left-hand side micrograph) and the distribution maps of the elements in 10CrMo9-10 steel after operation (right-hand side micrographs).

Figure 3. Positions of the microindentations in the 10CrMo9-10 steel.
As the carbides segregated preferentially at the grain boundaries, especially the rims of the grains were depleted in carbon and alloying elements. Consequently, the growth of carbides, their spheroidization and coagulation contributed to the nucleation of voids (micropores) at the grain boundaries and at the interfaces between the matrix and carbides.

3.2. Steel 13CrMo4-5

Before exploitation, the 13CrMo4-5 steel had a ferritic-bainitic/perlitic microstructure with a relatively high amount of ferrite (figure 4, upper left panel). The tensile strength, yield strength and impact strength of 13CrMo4-5 steel before operation were 582MPa, 321MPa and 34J, respectively. The operation led to the degradation of the perlite/bainite and to the precipitation of carbides (figure 4). Nevertheless, no creep micropores were observed in 13CrMo4-5 steel, after it was exploited for 23,000 h at 550°C. The amount of the carbide precipitates is lower than in the steel 10CrMo9-10. Their size and shape differ for perlite/bainite grains and for austenite grains. In the perlite/bainite grains, larger precipitates form than in the ferrite grains (figures 5 and 6). Large precipitates have a form of carbide plates and occur mainly in the areas of partly degraded perlite/bainite. Small precipitates occurring in ferrite grains are rather spherical. The EDX analysis in TEM (figure 5) revealed that the large carbide precipitates in perlite/bainite are rich on iron and chromium, whereas the smaller precipitates in ferrite have additionally higher Mn and Mo contents. The SAED in TEM identified the precipitates in perlitic/bainitic areas as M_{23}C_6 and M_{7}C_3 carbides (figures 6a, 6b). Taking into account the results of the local chemical analysis, the corresponding phases can be described as (Cr, Fe)_{23}C_6, (Cr, Mn)_{23}C_6, Cr,C_3 and (Fe, Mn)_7C_3. Inside the ferritic grains, carbides of types M,C, i.e., Fe,C, (Fe, Mn)_7C_3, (Fe, Cr)_7C_3 and M,C, i.e., (Fe, Mo)_6C_3 prevail (figures 6c, 6d).

The microhardness of the 13CrMo4-5 steel before exploitation was 242.2 HV0.1, after exploitation between 222.8 and 238.6 HV0.1 (figure 7). Both, the decrease of hardness after operation and the differences in the hardness across the pipe wall were much smaller than for the steel 10CrMo9-10. Comparing the hardness of both steels, one can see that the microstructure of the steel 10CrMo9-10 containing more Cr and Mo degrades much more than the microstructure of the 13CrMo4-5 steel. The microstructure of the steel 10CrMo9-10 is mainly affected by the segregation of carbides to the grain boundaries. The originally bainitic microstructure transforms to the ferritic/bainitic one, and the carbides segregated at the grain boundaries contribute to the

| Steel     | R_m MPa | R_p MPa | KV J |
|-----------|---------|---------|------|
| 10CrMo9-10 steel Before operation | 605     | 345     | 156  |
| After operation | 522     | 305     | 112  |

Table 2. Collation of basic mechanical properties of 10CrMo9-10 steel.

Figure 4. The microstructure of the 13CrMo4-5 steel before and after exploitation as seen by optical microscopy.
formation of micropores. Serious corrosion of the grain boundaries from the flue gas side was observed for this steel (figure 3—outside).

At the same time, it could be claimed that the element made of the 13CrMo4-5 steel operated 23,000 h at 550 °C met the applicable requirements provided in the EN standard [21]. The obtained results of investigations on $R_m$, $R_e$ and impact strength are shown in table 3. Mechanical properties such as $R_m$, $R_e$ and KV of 13CrMo4-5 steel after operation were 32, 12 and 3 units lower, respectively, compared to the material as delivered.

**4. Discussion**

Chromium is the basic alloying component in steels intended for operation at elevated temperatures, however, its impact on the properties is clear only if it exists in combination with such elements as e.g. Ni, Mo, V, or Mn. Chromium forms in steel a few varieties of permanent carbides, where the iron and chromium atoms can
substitute each other. The solution heat treatment of martensite and ferrite, which occurs after steel quenching or normalising, causes that new carbides precipitate during the next tempering or operation at elevated temperatures. The chemical composition of previously precipitated carbides changes, their morphology as well. The long-term operation results not only in the formation of new carbides, both on grain boundaries and inside the grains, but also in coarsening of existing carbides. During the operation also spheroidisation of plate-like carbides proceeds, which become spheroidal and ellipsoidal in shape. Increasing amount of M$_{23}$C$_{6}$ type carbides in long-time operated components, as compared with the initial state, is related to the ‘in situ’ transformation of M$_{3}$C and M$_{7}$C$_{3}$ carbides to the M$_{23}$C$_{6}$ carbides. The increase of the size of the carbides and their preferred precipitation on the grain boundaries are two of the reasons for the increase in brittleness and decrease of mechanical properties.

There are many research papers related to carbides precipitation and transformation both during the steel heat treatment and during long-term operation of elements at elevated temperatures [22–25]. Liu et al [22] investigated various austenitization conditions (holding time, temperature and the subsequent cooling rate), which were used to clarify the effect of normalizing conditions on the formation of the M$_{3}$C phase. In spite of various austenitization conditions applied, it was found that the precipitation of M$_{3}$C phase depended only on the cooling rate applied. Furthermore, the precipitation of M$_{3}$C phase occurs before the onset of the martensite transformation. The evolution of precipitate phases in 9CrMoCoB steel after tempering at 650 °C for different times was investigated by the authors of paper [23]. They found that the needle-like M$_{3}$C carbides could precipitate during both the air cooling process after austenitization and the early stage of tempering. After tempering for 15 to 120 min, fine M$_{2}$X particles were observed. The precipitation and growth of M$_{2}$X were derived from partial consumption of M$_{3}$C carbides. After tempering for 50 h, M$_{2}$X disappeared, while the rod-like M$_{7}$C$_{3}$ carbides were observed to precipitate independently of M$_{3}$C precipitates formed earlier. After tempering for 100 h, only M$_{23}$C$_{6}$ carbides remained, which number, density, and size kept increasing throughout 30 min to 100 h owing to their high thermostability. Dong et al [24] identified four kinds of precipitates (M$_{3}$C, M$_{7}$C$_{3}$, M$_{23}$C$_{6}$ and M$_{4}$C$_{7}$) at different tempering temperatures. At the tempering temperatures ranging from 200 to 400 °C, M$_{3}$C precipitated first. When the tempering temperature was 500 °C, some M$_{3}$C carbides were replaced by M$_{7}$C$_{3}$ and M$_{23}$C$_{6}$ precipitated. When the tempering temperature exceeded 600 °C, M$_{3}$C disappeared, and some M$_{2}$C were transformed into M$_{2}$C$_{3}$. At different tempering temperatures, two types of MC carbides existed steadily. It was suggested that the mechanisms of M$_{3}$C and two types of MC nucleation would be the same.
agree with a type of ‘separate nucleation’, and the mechanisms of the M₇C₃, M₂₃C₆ and M₂C₃ nucleation are likely to be of ‘in situ transformation’ type [24]. Two types of MC carbides were found to be stable phases existing over a wide temperature range [24]. The precipitation sequence of other carbides at different tempering temperatures can be expressed as follows [24]:

\[ M_2C \rightarrow M_2C + M_2C + \text{M}_{23}C_6 \rightarrow M_2C + \text{M}_{23}C_6 + M_2C_3. \]

The following sequence of carbides precipitation is typical for the 13CrMo4-5 steel [25]:

\[ M_2C \rightarrow M_7C_3 + M_2C + M_7C_3 + \text{M}_{23}C_6 \rightarrow M_7C_3 + M_2C + \text{M}_{23}C_6 + M_6C (+ M_2C_3). \]

In the 13CrMo4-5 steel tested, inside the ferrite grains, the M₇C₃(Fe,Cr)(Fe,Mn),Cr and M₆C(Fe,Mn)₃ carbides were identified. In turn, the M₂₃C₆((Cr,Fe)₂₃C₆, (Cr,Mn)₂₃C₆) and M₃C₆((Fe,Mn)₃C₃, Cr₃C₄) carbide types occurred in perlitic/bainitic areas.

According to [25], in the case of 10CrMo9-10 steel, molybdenum carbides M₇C₃ precipitate in the pro-eutectoid ferrite, and then—during slower cooling—eutectoid appears (ferrite + fibrous M₇C₃ carbides). M₂₃C₆ precipitates during slow cooling between the range of eutectoid and bainitic transformation. The existence of a large amount of Cr and Mo at a small carbon content in steel makes the pearlite occurrence impossible. In this steel cementite can exist only in bainite. During isothermal transformation of austenite \( T = 600 \, ^\circ \text{C} \)–800 \( ^\circ \text{C} \) ferrite originates at first, and only after a longer period M₂C carbides precipitate inside ferrite, while M₂₃C₆ on grain boundaries. Then almost simultaneously eutectoid originates, consisting of ferrite and fibrous M₂C carbides. After the end of transformation, M₇C₃ and M₆C carbides may appear after a long time [25].

In the tested 10CrMo9-10 steel, mainly M₇C₃ carbides occur inside the former austenite grain after exploitation. However, at the grain boundaries, in addition to M₇C₃ carbides, there are also M₂₃C₆ carbides. There are also small M₇C₃ carbides. Local chemical analysis confirmed the presence of (Cr, Mo)₂₃C₆(Fe, Mn)₂₃C₆, Cr₃C₄, (Mn, Fe)₃C₄, (Fe, Cr)₃C and (Fe, Mn)₃C.

A much smaller amount of carbides in ferrite grains close to boundaries and a higher amount of carbides on grain boundaries is a characteristic feature of the structure in the post-operation condition. Strong depletion in carbides of grain areas close to boundaries as against the grain inside indicates an accelerated process of carbides coagulation and its slightly different course. Carbon, because of very high surface activity, diffuses from supersaturated ferrite areas, in which carbides dissolved, to grain boundaries instead of other, more stable carbides, like in a normal coagulation process. Atoms of carbide forming elements diffuse behind carbon atoms to grain boundaries, as a result of which new carbides precipitate on grain boundaries or carbides previously precipitated there grow and change the chemical composition.

The power equipment durability is limited mainly through changes of properties, caused by the occurring structural processes such as carbides precipitation and transformations, carbides morphology changes, decomposition of pearlite/bainite areas, matrix depletion mainly in chromium and molybdenum, as well as depletion of boundary areas in precipitations or phosphorus segregation to grain boundaries.

Despite decreased mechanical properties of both steels in the post-operation condition they satisfy requirements set by the EN standard [21].

5. Summary

The long-term operation of the steels 10CrMo9-10 and 13CrMo4-5 in a steam heater leads to serious changes in their microstructure. These changes concern mainly the diffusion of alloying elements out of the bainite, the formation and coagulation of carbide precipitates at the grain boundaries and the partial transformation of original bainite to ferrite. These processes cause a gradual exhaustion of the material, which leads to the decay of the original steel microstructure and to the degradation of the steels strength. In both steels under study, a higher degradation was observed on the flue gas inflow side. This degradation is associated with a significant crevice corrosion, which propagates along grain boundaries. In the steel 10CrMo9-10 operated at 480 \( ^\circ \text{C} \), individual creep voids were visible after 130,000 h. Occasionally, the voids form chains are formed. Typical precipitates in the steel 10CrMo9-10 were chromium and molybdenum-rich carbides M₂₃C₆, M₇C₃ and M₆C. In the steel 13CrMo4-5, the typical precipitates at the grain boundaries were manganese-containing carbides M₂₃C₆ and M₆C, within the grains the carbides of types M₇C₃ and (Fe, Mo)₃C.

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