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MICROSTRUCTURE AND MECHANICAL PROPERTIES OF CRMOV STEEL AFTER LONG-TERM SERVICE

The paper presents the results of research on the microstructure and mechanical properties of 12HMF steel after long-term service. The investigated material was taken from a pipeline with circumferential welded joint after 419 988 hours of service at the temperature of 490°C, steam pressure 8 MPa. Performed research has shown that the 12HMF steel after service was characterized by a typical microstructure for this grade of steel, that is a ferritic-bainitic microstructure without any visible advanced processes of its degradation. The investigation of mechanical properties has shown that the examined steel after service was characterized by a very low impact energy KV, and yield strength lower than the required minimum. Whilst tensile strength and yield strength determined at elevated temperature was higher and similar to the standard requirements, respectively. It has been proved that the main cause of an increase in brittleness and a decrease in yield strength of the examined steel should be seen in the segregation of phosphorus to grain boundaries and the formation of precipitate free zones near the boundaries.

1. Introduction

Low-alloy CrMoV steels designed for work at elevated temperature belong to a group of the basic construction materials used for manufacturing power devices, such as: pipelines of live steam and reheat steam, mostly. The CrMoV steels were characterized by good strength properties and plastic properties in the range of steam temperature up to 560°C. Their creep strength was also higher than that of 10CrMo9-10 steels. Long-term service of steel at elevated temperature in creep conditions leads to its degradation through a number of changes running in the microstructure, contributing to a decrease in functional properties. In consequence, it can lead to damages in elements or constructions [1, 2]. Therefore, it is extremely important to perform thorough and comprehensive diagnostic tests whose aim would be to assess the general condition of construction elements. This is especially needed since the national power system is largely used up, and more than 90% of power units has exceeded the calculated time of operation, amounting to 100 000 hours, as well as 200 000 hours [1, 3]. Diagnostic tests can be carried out using the methods of nondestructive testing or/and the destructive testing on the representative segments taken from the elements of pressure devices. The

results of the tests obtained at a given stage of service allow determining the so-called degree of material exhaustion, on the basis of analysis of the microstructure images, morphology of precipitates and mechanical properties [1, 4]. To make it possible, building and expanding data bases and material characteristics is necessary, not only for the materials used in the power industry, but also for the joints after service in creep conditions. The article presents the results of research on the microstructure and mechanical properties of circumferential welded joint after long-term service.

2. Material and methodology of research

The material for research was a segment of a pipeline with the size: \varnothing 323 x 32 mm, after long-term service at the temperature of 490°C, steam pressure 8 MPa, and time of service amounting to 419 988 hours. The segment was taken from a pipeline running from a fresh steam collector to a distributing and cooling station. The chemical composition of 12HMF steel is presented in Table I.

The observation and registration of the microstructure images was performed using an optical microscope, Axiovert

TABLE 1

Chemical composition of the 12HMF steel, % wt

C	Mn	Si	P	S	Cr	Ni	Mo	V	Cu	Almet
0.13	0.58	0.29	0.012	0.017	1.09	0.08	0.27	0.20	0.14	0.021

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25 (OM), and scanning electron microscope, Jeol JSM 6610LV (SEM), on the conventionally prepared metallographic specimens etched with nital. Identification of the precipitates was performed by means of transmission electron microscope, Philips 301G, using extraction carbon replicas. The tests of mechanical properties included: measurement of hardness with Vickers method, using hardness testing machine Future-Tech FV-700, static test of tension carried out using the MTS-810 tester, and the Charpy's test of impact energy, on the standard test pieces with V-notch cut. Static test of tension at elevated temperature was performed using the Instron 8502 tester. Due to the fact that the properties of the examined element before the service were unknown, the obtained results of tests of mechanical properties were compared with the requirements stated in the standard [5]. In the case of the impact energy test, the value of 27 J was assumed as the criterion of the minimum ductility.

3. Microstructure of CrMoV steel after service

The microstructure of the investigated steel was ferritic–bainitic with the dominant quasipolygonal ferrite amount (Fig. 1). The estimated volume fraction of particular microstructure components was the following: quasipolygonal ferrite – ca. 60%, polygonal ferrite – ca. 30%, bainite – ca. 10%. Quasipolygonal ferrite is ferrite with a large amount of fine dispersive carbides precipitated inside the grains. In the microstructure image with the optical microscopy zoom, this type of ferrite can be seen as grains of grey colour. Quasipolygonal ferrite, at the moment of being formed, has the chemical composition similar to the chemical composition of austenite, out of which it is formed. As a result of carbon supersaturation, during cooling after the austenitization process, and mostly after the following tempering, numerous fine dispersive carbides are precipitated. The colour of polygonal ferrite in the image obtained with optical microscopy is bright. At the forming stage, the chemical composition of ferrite is similar to the equilibrium one, therefore, it does not contain carbides, or it contains some single precipitations [2]. The size of ferrite grain, determined using illustrated models [6], amounted to 5, which corresponds to the mean diameter of grain: 62.5 μm .

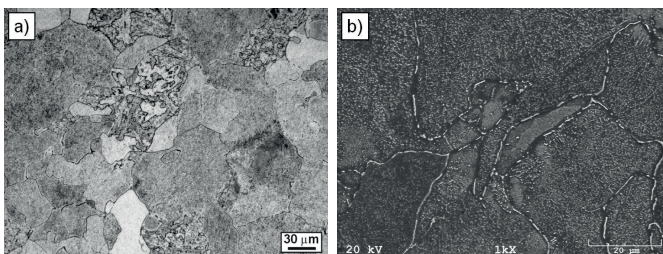


Fig. 1. Microstructure of 12HMF steel after long-term service: a) OM; b) SEM

On the boundaries of ferrite grains, not only single but also numerous precipitations of diverse size were observed, forming in some areas the so-called “continuous grid of precipitates”. Precipitation of carbides on grain boundaries

impedes grain gliding against each other, and at the same time contributes to an increase in the microstructure strength, however, at the expense of lowering its ductility. In CrMoV steels in the as-received condition (after the heat treatment), a number of carbides of different thermodynamic stability can be observed (M_3C , M_2C , M_7C_3 , $M_{23}C_6$, MC). Their type and amount depends on the chemical composition (amount of carbon and carbide-forming elements) and the heat treatment parameters [7-10]. Stability of carbides in the serviced low-alloy CrMoV steels is very high. Researchers have noticed the occurrence of all types of carbides in the serviced steels, even after more than 150 000 hours of work at elevated temperature above 500°C [11-13]. Nevertheless, during the service, not only the enrichment of precipitated carbides with chromium and molybdenum, but also the changes in the morphology and quantitative fraction could be observed. Moreover, during the service of CrMoV steel, precipitation of M_6C carbides and compound complexes of precipitates, referred to as „H – carbides”, were seen [12, 13]. Performed identifications have shown the occurrence of the following precipitates in the examined steel after service: M_3C , M_2C , M_7C_3 and MC . Precipitates of M_2C and MC type were revealed inside quasipolygonal ferrite grains, whilst the M_7C_3 carbides were observed mostly on the boundaries of grains and in bainite. In bainite, also the M_3C carbides were noticed. Example of the morphology of carbides in the investigated steel is shown in Fig. 2.

However, performed thermodynamic calculations by means of TCW program have shown that the equilibrium carbides for the examined cast steel at room temperature are as follows: MC , $M_{23}C_6$, M_6C . According to studies [7, 12], in low-alloy CrMoV steels of chemical composition containing below 3% chromium mass, the $M_{23}C_6$ carbides are metastable precipitates.

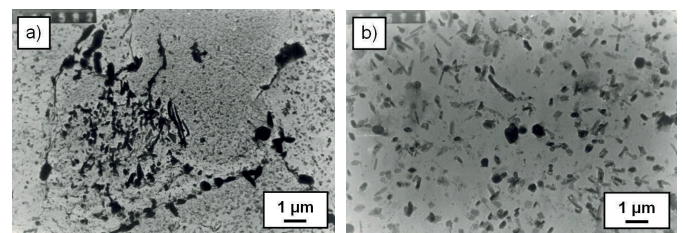


Fig. 2. Morphology of carbides in the examined steel: a) in the bainite area and on the grain boundaries, b) inside ferrite grains, carbon extraction replica, TEM

Moreover, another studies [11] prove that the $M_{23}C_6$ carbides during the service of CrMoV steel are subject to transformation into more thermodynamically stable M_7C_3 carbides. Nevertheless, as shown in the monograph [14], in the CrMoV steels serviced at the temperature of about 540°C, the dominant precipitation was $M_{23}C_6$ carbide. In the Authors' opinion, in the low-alloy CrMoV steels, the morphology of carbides is influenced not only by the chemical composition of steel or its heat treatment parameters, but also by the parameters of service. The characteristic feature observed in the low-alloy steels after long-term service, as well as in the examined steel, was the occurrence of carbide free zones near the grain boundaries (Fig. 3).

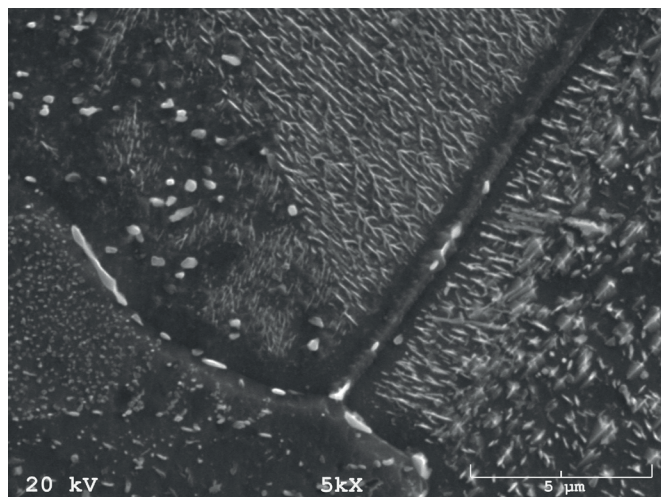


Fig. 3. Precipitate free zone near the boundaries of ferrite grains

According to researchers [2, 15, 16], the formation of these zones is connected with the processes of precipitation and growth of carbides on the boundaries of grains, and the width of this zone is dependent on both: the service parameters and chemical composition of the steel [2, 16]. The depletion of precipitates in these areas near the grain boundaries decreases the strength of these areas and constitutes a deciding factor responsible for the slowly progressing decline of strength properties throughout the service time.

The observations of the microstructure of the investigated steel haven't revealed any initiating processes of internal damage or microstructure discontinuity.

4. Mechanical properties of CrMoV steel after service

The studies of mechanical properties have shown that the CrMoV steel after service was characterized by very low impact energy KV, which was over five times as low, compared to the required minimum of 27 J (Table II). Performed fractographic tests have proved that the examined steel was cracking with the brittle transcrystalline cleavable mechanism (Fig. 4). Moreover, on the fracture, numerous secondary cracks were observed. They ran on the boundaries of grains. The presence of intergranular secondary cracks proves the brittleness and softening of the boundaries.

Low impact energy is connected with the brittle fracture transition temperature, shifted to positive temperatures, which amounted to + 65°C for the criterion of 27 J. Shifting the temperature of brittleness threshold for the examined steel to positive temperatures indicates the deformation ability of

the steel at room temperature. The decrease in the impact energy and growth of the brittle fracture transition temperature in long-term serviced low-alloy CrMoV steels should be associated with an increase in the number and size of the carbides precipitated on the boundaries of ferrite grains.

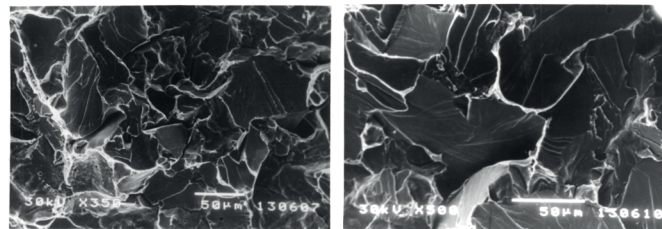


Fig. 4. Fractography of the fracture in the examined steel

The dependence between the precipitates on the grain boundaries and the growth of brittleness in the low-alloy steels has been discussed inter alia in the publications [15, 17]. However, according to studies [18], brittleness of CrMoV steels serviced below the temperature of 540°C is not connected with the precipitations on the boundaries of grains. The above shows that the main cause for the growth of brittleness in the investigated steel can be the increase in the concentration of phosphorus on the boundaries of grains. Phosphorus in low-alloy steels/cast steels, as proved with the data [19, 20], is one of the most damaging additions, mostly responsible for the growth of brittleness in these materials. The increase in the phosphorus concentration in the areas near the boundaries contributes to a decrease in their cohesion, which in consequence leads to the drop of ductility and growth of brittle fracture transition temperature. The higher the concentration of phosphorus on grain boundary, the lower the service temperature and the higher the content of phosphorus in the serviced steel/cast steel [19, 21-23].

The strength properties in the examined steel after service (Table II), determined at room temperature, have shown that the apparent yield stress $YS_{0.2}$ was lower than the required minimum by around 14%, whilst the tensile strength TS fulfilled the standard requirements for the pipe material [5]. The value of elongation A also met the requirements stated by this standard. Hardness of the investigated steel after service amounted to 174 HV30.

The strength properties determined at room temperature were similar to the minimum required ones (Table III). The observed decrease in the value of yield strength in the examined steel should be associated with the presence of carbide free zones in the microstructure.

TABLE 2

Mechanical properties of the examined steel after service

$YS_{0.2}$ MPa	TS MPa	El. %	RA %	KV J	KCV J/cm ²	HV30
254	528	33	45	5	6.25	174
min. 295	440 ÷ 640	min. 21*; min. 19**	---	min. 27 J	---	

* - transverse samples; ** - longitudinal samples

TABLE 3

Mechanical properties of the examined steel at elevated temperature

Temperature of testing	YS _{0.2} MPa	TS MPa	El. %
450	198	386	26.6
500	184	328	33.2
550	174	275	36.4
Requirements according to [5]	YS _{0.2} ⁴⁵⁰ min = 206 MPa; YS _{0.2} ⁵⁰⁰ min = 186 MPa		

As literature data show [16, 24-28], the presence of precipitate free zones in metallic alloys causes not only a decrease in the value of yield strength or tensile strength, but also results in the fall of creep resistance. Moreover, the literature sources [15, 29] also attribute the gradual decrease in strength properties during the service of low-alloy CrMoV steels to the reduction of strengthening effect: the one related to solution (matrix depletion of carbon atoms and carbide-forming elements) and the one related to precipitation (process of coagulation and transition of carbides).

5. Conclusions

Performed microstructural research has shown that in the investigated steel, in spite of the very long service time declared, the advanced processes of microstructure degradation were not observed. It can result from the low temperature of service of the examined element, insignificantly higher than the temperature limit estimated for 12HMF steel, amounting to around 480°C.

Nevertheless, long-term service of 12HMF steel has mostly contributed to the growth of brittleness (impact energy decrease) and the related shift of nil ductility temperature to positive temperatures, as well as faster decrease in the yield strength value in comparison with other strength properties. The above changes are connected with the precipitate free zones observed in the microstructure and the growth of phosphorus concentration that probably takes place in the areas near the boundaries.

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