Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 17
ISSUE 1-2
July-August
2006

Properties and microstructure of 12% Cr-W steels after long-term service

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Received 15.03.2006; accepted in revised form 30.04.2006

Materials

ABSTRACT

Purpose: The purpose of the research was to identify the influence of long-term exposition on stability of the microstructure and properties of new ferritic steels containing 12% Cr with W addition.
Design/methodology/approach: The research allowed the identification of microstructural changes that take place during long-term operation and their influence on the mechanical properties. The examinations were conducted on superheater tubes (HCM12 and HCM12A steel) after 20 and 30 thousand hours of exposition. The scope of the research encompassed a microstructural analysis with the use of LM, SEM and TEM and measurement of hardness and strength at an ambient temperature and at 600ºC.
Findings: It was found that the steels showed high stability of structures and mechanical properties. The main symptoms of degradation are connected with the decomposition of martensite areas, the precipitation of $M_{23}C_6$ carbides and Laves' phases, and the processes of recrystallization and recovery. The level of all mechanical parameters was still satisfactory after 30,000 hours of operation.
Research limitations/implications: The discussed research proves high stability of the microstructure and properties of the investigated steels, however it necessary to identify the mechanisms of structure degradation and, in consequence, of adjusting the mechanical properties below the values required. It is therefore necessary to continue the investigations after successive periods of operation.
Practical implications: The results obtained allow the determination of the degree of life-time lost of the investigated high-chromium steels and specification of the time of safety operation.
Originality/value: The results obtained are valuable contribution to the development of new steels for the power industry. They enable the identification of the degradation mechanisms in steels of new types, which enhances the durability and safety of boilers' operation.
Keywords: Metallic alloys; Methodology of research; Electron microscopy; Residual life analysis

1. Introduction

The development of high-chromium martensitic steels is dated back to the early 40s of 20th century, when England began searching for new materials for the production of gas turbine disks and blades. The result of those research activities was the production of H46 and FV448 steels of enhanced creep resistance. At the same time, in the USA, AISI-422, Allegheny Ludlum 419 and Lapelloy steels were used for turbine blades, whereas in Europe, HT-9 and EM-12 [1] steels were widely applied. Steels of that type constitute an intermediate material between low-alloy and austenitic steels. The low-alloy T22 steel shows high heat conduction, excellent resistance to scale drop-off and high resistance to SCC cracking. At the same time, however, it shows low resistance to corrosion in a sulphur environment and very low strength resistant at high temperatures. The austenitic TP321H steel is characterized by great high-temperature strength and resistance to corrosion, but shows a tendency to scale exfoliation and has insufficient heat conductivity. Therefore, there is a need for the development of new high-chromium steels of higher durability and weldability which could substitute austenitic steels [2]. Initially, various types of high-strength steels were developed, containing 9% Cr, e.g. HCM9M. They showed, however, limited resistance to corrosion. A type of steel widely applied for components operating in high-temperature conditions is the X20CrMoV121 containing 12% of chromium. It does not show, however, satisfactory strength under such conditions and has limited weldability due to a relatively high carbon content. It became necessary then, to search for new steels with a 12% Cr content, which would not have the above-mentioned drawbacks [3-14]. Sumitomo Metla Industries Ltd. elaborated a new type of 12% Cr steel of enhanced resistance and weldability [15]. The next step in the evolution of those steels was the HCM12A, where Mo was replaced by tungsten. Another steel representing this group is P92. These steels show better strength properties than HCM12 and P91 steels, respectively.

2. Description of experiments, methodology and materials

Examinations were carried out martensitic steels grades containing 12% Cr with tungsten addition such as HCM12 and HCM12A. Materials subjected to testing, i.e. elements made new generation creep-resisting steel grades with the following dimensions:

- ϕ38×4 mm made of HCM12 steel
- ϕ38×6,3 mm made of HCM12A steel

This article shows only the selected results of strength and metallographic examinations within the field of assessment of base material properties and structure stability of steam superheater coils elements made of HCM12 and HCM12A:

- after 20 000 and 30 000 hours of operation in actual operating conditions of boiler no. 7 in Bełchatów Power Plant.

2.1. Characterization of microstructure

The HCM12 steel after 20 thousand hours of operation is characterized by a two-phase structure of tempered martensite and δ–ferrite in the amount of up to 30%, with carbides precipitation on ferrite grain boundaries and inside ferrite grain (Fig. 1).

Hardness of this material is 208 HV. The substructure of the HCM12 steel is characterized by the occurrence of lath martensite and δ-ferrite (Fig.2). A long-term operation causes both intensive carbides precipitation and processes of recovery and polygoniztion in the steel structure. Precipitations of $M_{23}C_6$ are uniformly distributed throughout primary austenite grain boundaries and throughout martensite laths (Fig.3); whilst areas of δ-ferrite contain fine-dispersion precipitations of VC and acicular precipitations of $M_{23}C_6$.

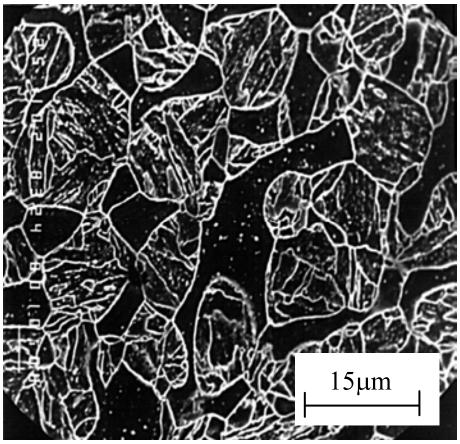

Fig. 1. HCM12 steel microstructure after 20 thousand hours of operation

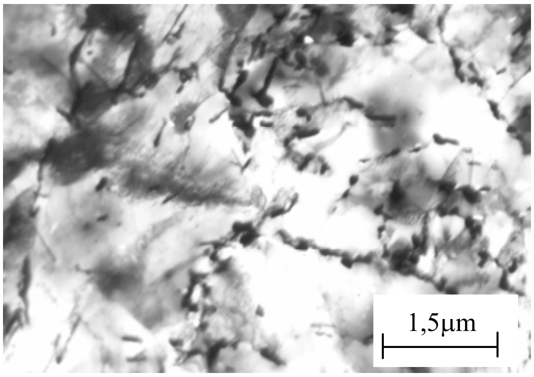

Fig. 2. Two-phase regions of tempered martensite and δ-ferrite

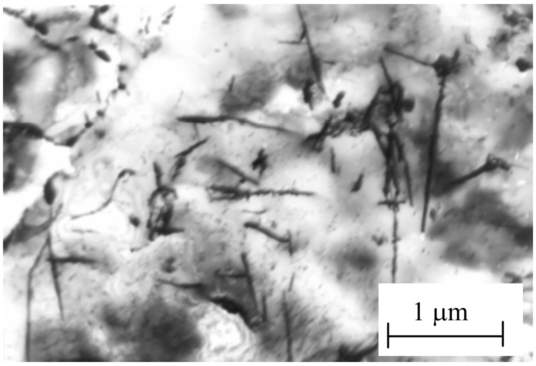

Fig. 3. δ-Ferrite with acicular precipitations of $M_{23}C_6$

The HCM12A steel after 20 thousand hours of operation shows a structure of tempered martensite with an insignificant amount ferrite δ (<5%) (Fig. 4). In addition, few precipitations of $M_{23}C_6$ carbides were observed on grain boundaries. The material shows hardness of 223 HV. The substructure of the HCM12A steel after 20 thousand hours of operation is characterized by well-shaped polygonal subgrains (Fig.5), inside of which very low dislocation density is observed, which results from the action of temperature and time.

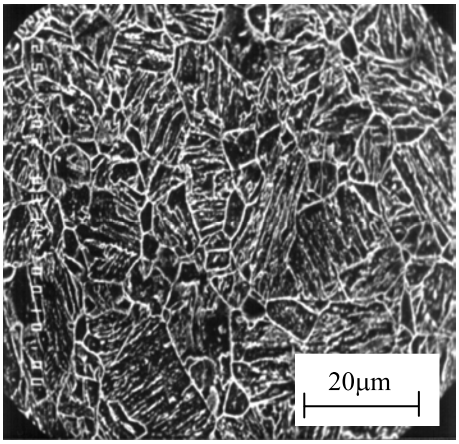

Fig. 4. HCM12A steel microstructure after 20 thousand hours of operation

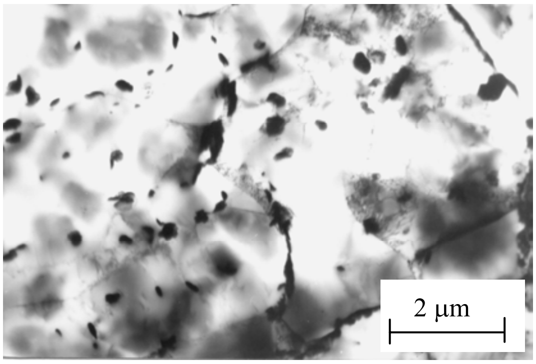

Fig. 5. Subgrain structure with multiple carbide precipitations along grain boundaries

Precipitation of $M_{23}C_6$ carbides was noticed mostly on equiaxial subgrain boundaries.The precipitating carbides had longitudinal and coagulated shapes. In the vicinity of the coagulated $M_{23}C_6$ carbide precipitations, elongated particles of Laves phases were observed (Fig. 6).

The image of such phases, however, was rare and the elongated precipitations were frequently particles of the $M_{23}C_6$. carbides. Precipitations of MX type occurred inside the subgrain.

Metallographic examinations of the HCM12 steel after 30000 hours of operation showed a relatively low influence of the operation time on the microstructure of the investigated steel. In case of the HCM12 steel, the structure of tempered martensite with delta-ferrite and numerous carbides inside grain predominated. Hardness of the examined steel amounted to 213 HV. The microstructure of the HCM12A steel after the same time of exposure did not undergo any considerable changes compared to its condition after 20000 hours of operation. In that case, the structure of tempered martensite with a small amount of delta ferrite dominated as well. Relevant measurements proved that after another 10000 hours of operation, the hardness amounted to 217 HV.

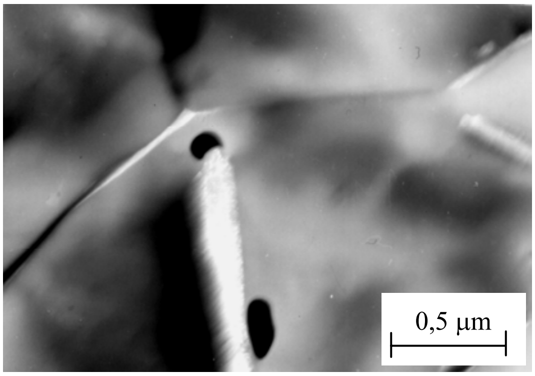

Fig. 6. Elongated precipitations of Laves phases in HCM12A steel. Dark field

2.2. Mechanical properties

Examined material consisted of steam superheater tubes made of HCM12 and HCM12A steel grades, with 38 mm diameter and wall thickness 4, 6,3 mm respectively. Examinations were carried out both at ambient temperature and at a temperature of 600ºC. Results of examination carried out at ambient temperature are shown in Tab.1, and results of those carried out at a temperature 600ºC are shown in Tab.2.

Table 1.
Results of static test at ambient temperature

	20 000h			30 000h		
	$R_{0,2}$ MPa	R_m MPa	A_5 %	$R_{0,2}$ MPa	R_m MPa	A_5 %
HCM12	450/ 454	716/ 691	20,5/ 21	434	673	19
HCM12A	600/ 503	774/ 651	40/ 22	554	664	20

Table 2.
Results of static test at temperature of 600ºC

	20 000h	30 000h
	$R_{0,2}^{600°C}$ MPa	$R_{0,2}^{600°C}$ MPa
HCM12	244/262	320
HCM12A	277/291	303

3. Disscussion

3.1. General remarks

The HCM12 steel is characterized by a two-phase structure of tempered martensite and δ–ferrite in the amount of up to 30%, with carbide precipitations along ferrite grain boundaries and inside the grain. A long-term operation induces intensive precipitation of carbides and the occurrence of recovery and polygonization processes. Precipitations of $M_{23}C_6$ are uniformly distributed throughout primary austenite grain boundaries and throughout martensite laths; whilst areas of δ-ferrite contain fine-dispersion precipitations of VC and acicular precipitations of $M_{23}C_6$.

The hardness level of this material is 208 HV. After 30000 hours of operation this steel shows a typical of this steel grade two-phase structure of tempered martensite with δ–ferrite, however, with a considerable fraction of carbide precipitations inside the grain. It was found that hardness is at a level higher than the required minimal value of 200 HV – 211 ÷ 214 HV. Similarly, the mechanical properties fulfill the requirements of relevant standards, i.e. the yield point at a room temperature is higher than 390 MPa; the yield point at 600°C is higher than 250 MPa and the elongation is lower than the minimum 20%. The HCM12A steel shows a structure of tempered martensite with little amount of δ–ferrite (<5%). Also, few precipitations of $M_{23}C_6$ carbides were observed on grain boundaries.

The substructure of the HCM12A steel is characterized by well-shaped polygonal subgrains, inside of which low dislocation density is observed, which results from the action of temperature and time. Precipitation of $M_{23}C_6$. carbides was noticed mostly on equiaxial subgrain boundaries. The precipitating carbides had longitudinal and coagulated shapes. MX precipitations occurred inside the subgrains.

The material shows hardness of 223 HV. After another 10000 hours of operation this steel shows a typical of this steel grade two-phase structure of tempered martensite with an insignificant amount of δ–ferrite and a small amount of carbide precipitations inside the grain, as well as hardness at a level higher than the required minimum value of the order of 200 HV, i.e. 214÷220 HV. The mechanical properties meet the requirements of relevant standards: the yield point at a room temperature is higher than 400 MPa; the yield point at 600°C is slightly lower than 310 MPa and the elongation equals the minimum 20%. In all the analyzed cases, the material shows a minimum degree of degradation connected with the occurrence of an insignificant number of carbides inside the grain and on grain boundaries.

The observed structure is correct and stable, the level of mechanical properties achieving values which considerably exceed the minimum values. Measurement of walls thickness also does not show effects of wear of the superheater tube. An analysis of the research results has shown that operation lasting 30 thousand hours did not influence much the microstructure or the level of properties of tubes made of the HCM12 and HCM12A .steels.

The investigated steels are characterized by great stability of microstructure at a temperature of ca. 585°C as was in experimental sections of the steam superheater coil.

4. Conclusions

- The new high-chromium HCM12 and HCM12A steels for the power industry, after 20000 and 30000 hours of operation, still present high stability of microstructure at a temperature of ca. 585°C, as was in experimental sections of the steam superheater coil.
- The main symptoms of the structure degradation process are connected with:
  - decomposition of martensitic regions,
  - precipitation of $M_{23}C_6$ carbides and Laves phases,
  - recrystallization and recovery processes.
- 30000 hours of operation did not substantially influence the level of mechanical properties which still fulfil the required criteria.

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