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Characterisation of properties and microstructural changes of 12% Cr-W steels after long-term service

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Properties

ABSTRACT

Purpose: Characterization of the influence of long-term exposition on microstructural stability and properties of new modified ferritic steels containing 12% Cr with W addition.
Design/methodology/approach: The examinations were made on samples from superheater tubes (HCM12 and HCM12A type of steel) after long term exposition (20 and 30 thousand hours). The major technique used to investigations are: microstructural analysis with the use of LM, SEM and TEM and measurement of hardness and strength at an ambient temperature and at 600ºC.
Findings: Investigated power plant steels exhibit high stability of microstructeres and mechanical properties. The main effects of degradation are related to the decomposition of martensite areas, the precipitation of $M_{23}C_6$ carbides and Laves' phases, and the processes of recrystallization and recovery. Results of mechanical examinations showed that main mechanical parameters was still satisfactory after 30.000 hours of operation.
Research limitations/implications: Presented examination showed that new type of power plant steels are characterized by high stability of the microstructure and properties, 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: Presented conclusion give the possibility to 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: This investigations 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: Residual life analysis; Electron microscopy; Metallic alloys

1. Introduction

The efficiency of conventional boiler/steam turbine fossil power plants is a function of temperature and pressure of the steam. Research to increase both has been pursued worldwide, since the energy crisis in the 1970s. The need to reduce CO_2 emission has recently provided an additional incentive to increase efficiency. Thus, steam temperatures of the most efficient fossil power plants are now in the 600°C range, which represents an increase of about 60°C in 30 years. It is expected that steam temperatures will rise another 50-100°C in the next 30 years.

The main enabling technology is the development of stronger high temperature materials, capable of operating under high stresses at ever increasing temperatures. The results of the review show that high strength ferritic 9-12Cr steels for use in thick section components are now commercially available for temperatures up to 620°C [1].

In the 1970s, there was considerable interest in the 9% chromium steels for components of the fast breeder nuclear reactor. On the basis of the familiar Fe9Cr1Mo steel used since the 1950s in petrochemical plant, an improved steel was developed by the Oak Ridge National Laboratory and subsequently incorporated into the ASTM specifications under the designation P91 (ASTM 1986). A remarkable increase in the stress rupture strength was achieved by the addition of 0.2% V, 0.06 Nb and 0.05 N. In Japan, a steel development programme of Nippon Steel led to the steel NF616, which is now designated P92 in the ASTM specification. With P92 a further increase in stress rupture strength was obtained by an addition of 1.8% W and a reduction of the Mo content from 1 to 0.5%. In the European COST (Co-operation in Science and Technology) Action 501, a similar 9% chromium steel was developed; this steel is designated E911, contains 1% Mo and 1% W, and offers similar stress rupture strength to P92 [2-5].

The need to obtain the optimum microstructure for high creep rupture strength and the requirement for improved steam oxidation resistance make contradictory demands on the steel composition. For satisfactory creep and stress rupture strength, Cr contents of around 9-10% allow the desired fully martensitic microstructure to be obtained. For adequate resistance to steam oxidation, Cr contents above 11% are necessary. The aim of the current steel developments is to raise the Cr content to 11-12%, and to add austenite stabilising elements to produce the fully martensitic structure. In this way, it is hoped that similar stress rupture strength levels to the 9% Cr steels can be reached at higher Cr contents in the range 11-12% [4]. Beyond 620°C, the 9%Cr steels become limited by oxidation resistance and 12%Cr steel and austenitic steels have to be used [6-17].

The chemical compositions of the new steels with 9% and 12% Cr contents are presented in Table 1 [16].

2. Description of experiments, methodology and materials

The basic tests were carried out martensitic steels 12% Cr type with tungsten addition (HCM12 and HCM12A). Examinations were carried out on pressure elements, after 20 000 and 30 000 hours of operation in actual operating conditions of boiler no. 7 in Bełchatów Power Plant (Fig. 1), with the following dimensions:

- ϕ38×4 mm made of HCM12 steel
- ϕ38×6.3 mm made of HCM12A steel

Specification of chemical composition of steel grades subject to examinations is shown in Table 1.

In this article only the selected results related to strength tests and metallographic investigations of steam superheater coils elements made of HCM12 and HCM12A within the field of assessment of base material properties and structure stability was presented.

Table 1.
Specifications of chemical composition of steel grades – in accordance with the requirements of standards – “norm” (upper lines of chemical compositions) and specification of chemical analyses of tubes on the basis of data coming form material certificates (lower lines of chemical compositions) [18]

Steel grade		Contents [%]														
		C	Si	Mn	P	S	Ni	Cr	Mo	W	Cu	V	Nb	Al	B	N
P91	Norm	0.08-0.12	0.2-0.5	0.3-0.6	<0.02	<0.01	<0.4	8.0-9.5	0.85-1.05	-	-	0.18-0.25	0.06-0.1	<0.04	-	0.03-0.07
	Cert.	0.10	0.45	0.44	0.015	0.001	0.13	8.16	0.94	-	-	0.21	0.07	0.04	-	0.06
P92	Norm	0.07-0.13	<0.5	0.3-0.8	<0.02	<0.01	<0.4	8.5-9.5	0.3-0.6	1.5-2	-	0.15-0.25	0.04-0.09	<0.04	0.001-0.006	0.03-0.07
	Cert.	0.094	0.21	0.46	0.015	0.002	0.26	8.84	0.47	1.72	-	0.21	0.07	0.04	0.038	0.06
HCM12	Norm	<0.14	<0.5	0.3-0.7	<0.03	<0.03	-	11-13	0.8-1.2	0.8-1.2	-	0.2-0.3	<0.2	-	-	-
	Cert.	0.1	0.26	0.53	0.028	0.02	-	11.93	1.01	1.02	-	0.24	0.4	-	-	-
HCM12A	Norm	0.07-0.14	<0.5	<0.7	<0.02	<0.01	<0.5	10-12.5	0.25–0.6	1.5-0.3	0.3-1.7	0.15-0.1	0.04-0.1	<0.04	<0.005	0.04-0.1
	Cert.	0.13	0.31	0.6	0.014	0.001	0.35	10.65	0.35	1.92	0.94	0.22	0.06	0.009	0.0009	0.061

2.1. Characterization of microstructure

The microstructural composition of HCM12 steel after 20 thousand hours of exposure in operation conditions is characterized by a tempered martensite and δ-ferrite (ca.30%), with precipitation of carbides in area of ferrite grain ferrite and grain boundaries (Figs. 2 and 3).

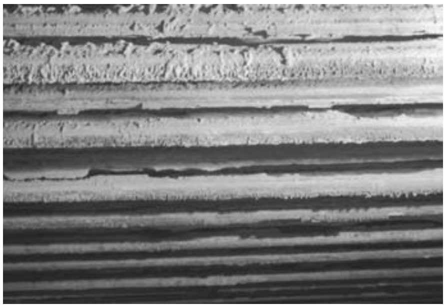

Fig. 1. General view of the P3 superheater tubes of BB-1150 boiler at Bełchatów Power Plant

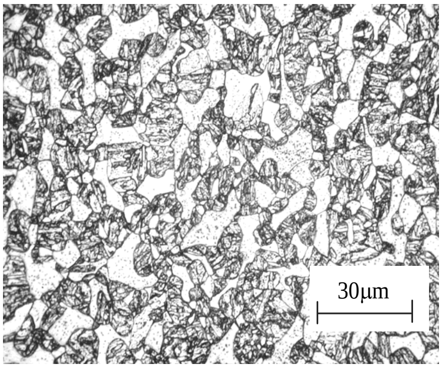

Fig. 2. HCM12 steel microstructure after 20 thousand hours of operation

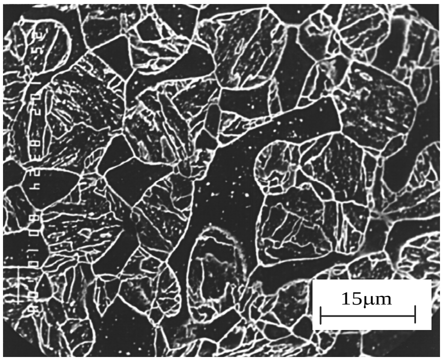

Fig. 3. HCM12 steel microstructure after 20 thousand hours of operation

The measurement of hardness showed that after 20000 h of exposure this value was 208 HV. The investigations of substructure showed that the steel exhibited a martensitic substructure with a δ-ferrite (Fig. 4). Long time high temperature exposition of investigated steel due to intensive effect of carbides precipitation and processes of recovery and polygoniztion in the steel substructure. TEM investigation showed that precipitations of $M_{23}C_6$ carbides are distributed uniformly throughout primary austenite grain boundaries and throughout martensite laths (Fig. 5). Furthermore fine-dispersion precipitations of VC (Fig. 6) and acicular precipitations of $M_{23}C_6$ (Fig. 7) were detected in δ-ferrite areas. The same type of investigations carried out on HCM12A type steel after 20 thousand hours of operation shows a similar substructure of tempered martensite but with an much smaller amount of ferrite δ (<5%) (Figs. 8 and 9). The detailed investigations of grain boundaries showed additionally presence of $M_{23}C_6$ carbides precipitations. In comparison to HCM12 steel the hardness measurement showed much bigger value of this parameter - 223 HV.

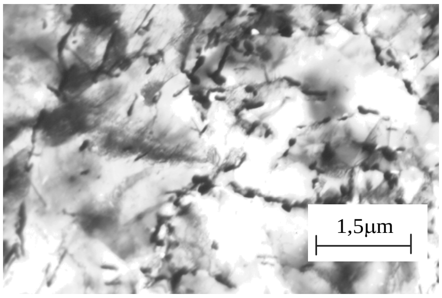

Fig. 4. Two-phase regions of tempered martensite and δ-ferrite

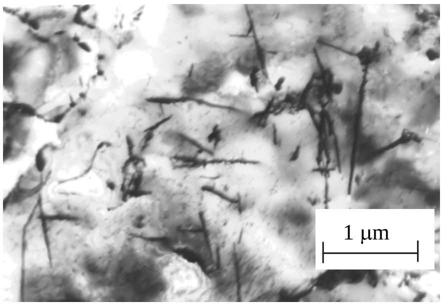

Fig. 5. δ-Ferrite with acicular precipitations of $M_{23}C_6$

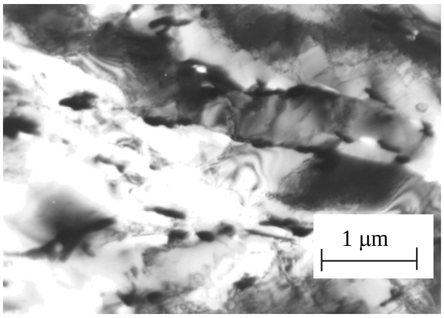

Fig. 6. Tempered martensite laths with $M_{23}C_6$ carbide precipitations of on grain boundaries

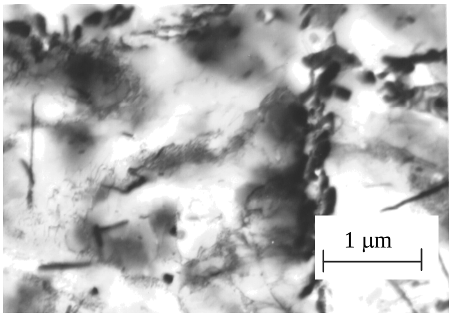

Fig. 7. Polygonal dislocation systems inside δ-ferrite regions and fine-dispersion precipitations of MX carbides

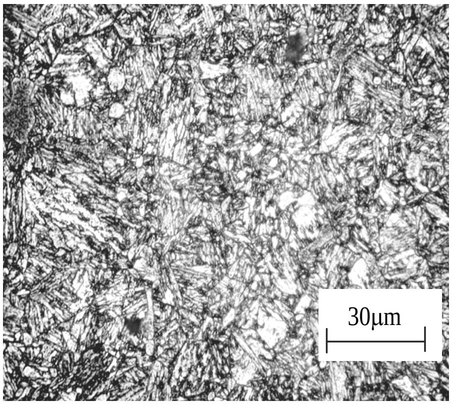

Fig. 8. HCM12A steel microstructure after 20 thousand hours of operation

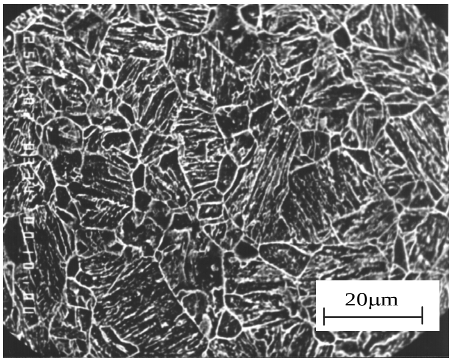

Fig. 9. HCM12A steel microstructure after 20 thousand hours of operation

The substructure TEM investigations of the second type of steel after the same time of exposure is characterized by well-shaped polygonal subgrains (Fig. 10). The detailed investigations of inside areas of grain exhibit that a very low dislocation density is observed.

This effect is a consequence of action of temperature and time. The presence of $M_{23}C_6$ carbides precipitation was noticed generally on equiaxial subgrain boundaries. The effect of coagulation of longitudinal in shapes carbides was observed as well. In the vicinity of the coagulated $M_{23}C_6$ carbide precipitations, elongated particles of Laves phases were observed (Figs. 11 and 12). 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.

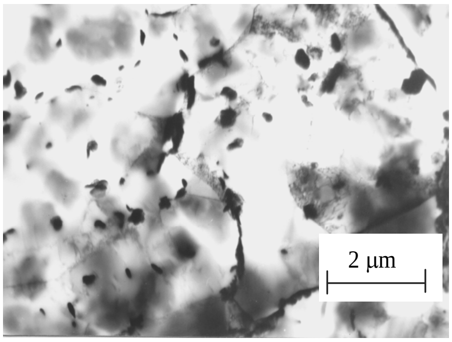

Fig. 10. Subgrain structure with multiple carbide precipitations along grain boundaries

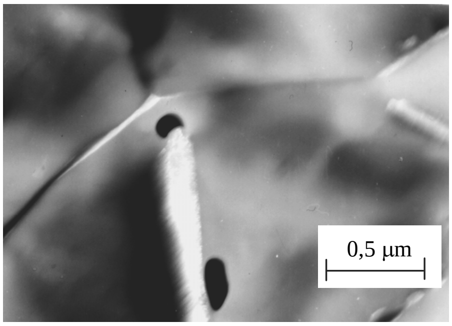

Fig. 11. Elongated precipitations of Laves phases in HCM12A steel (dark field)

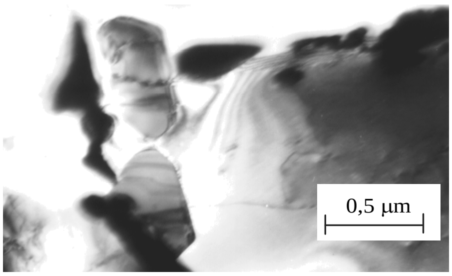

Fig. 12. M23C6 carbide precipitations in the HCM12A steel (bright field)

Detailed metallographic examinations of the HCM12 steel after next 10000h of operation (30000 hours) showed a relatively low influence of the exposure time on the microstructural changes. Tem observations confirmed that tempered martensite with delta-ferrite and numerous carbides inside grain are the predominated type of substructure in this case (Figs. 13 and 14). The value of hardness was 213 HV.

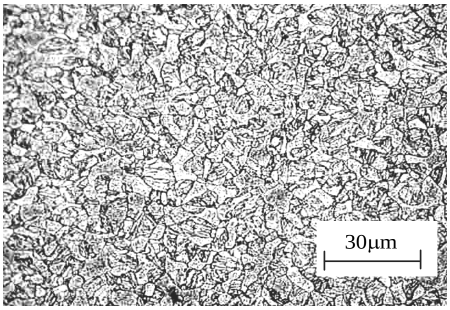

Fig. 13. HCM12 steel microstructure after 30 thousand hours of operation

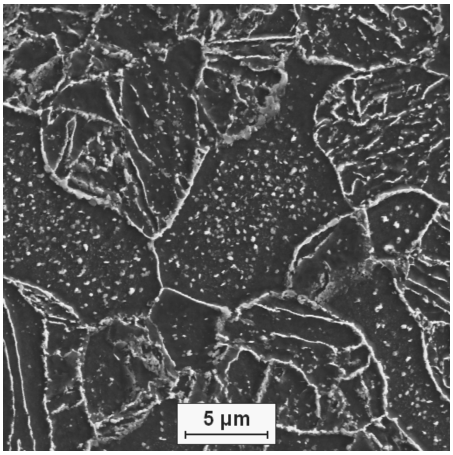

Fig. 14. HCM12 steel microstructure after 30 thousand hours of operation

The substructure investigation of HCM12 steel showed that in this case exists $M_{23}C_6$ carbides and some participation of Leves phases $Fe_2(Mo,W)$ type (Fig. 15). 30 thousand hours exposition induces intensive precipitation of carbides and the occurrence of recovery processes in the matrix (Fig. 16). In side grain was found dispersed MX carbides and small $M_{23}C_6$ precipitates (Fig. 17).

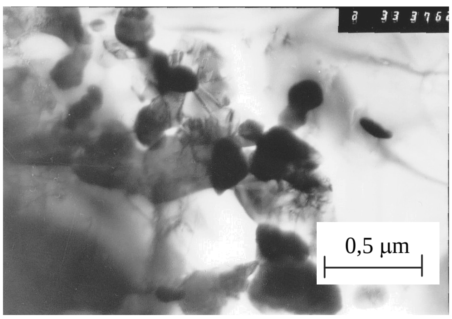

Fig. 15. Subgrain structure with $M_{23}C_6$ carbides and some participation of Leves phases $Fe_2(Mo,W)$ type precipitations

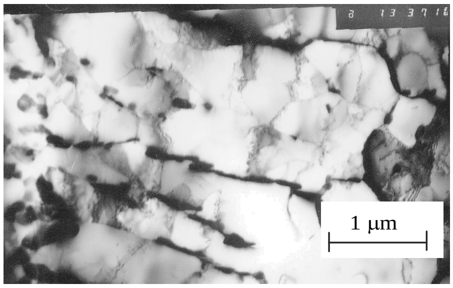

Fig. 16. Subgrain structure with intensive effect of precipitation of carbides and the occurrence of recovery processes in the matrix

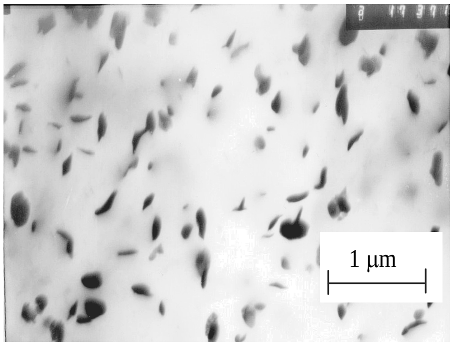

Fig. 17. MX carbides and small $M_{23}C_6$ precipitates inside of the grains

The same conclusion are after examination of the HCM12A steel microstructure after the another 10000 h of exposure. There was observed any considerable changes compared to its condition after 20000 hours of operation. In this case still the predominant type of structure is related to presence of tempered martensite with a small amount of delta ferrite. Relevant measurements proved that after another 10000 hours of operation, the hardness amounted to 217 HV. Apart from that, a slightly increased content of carbides was found in the area of martensite grain (Figs. 18 and 19).

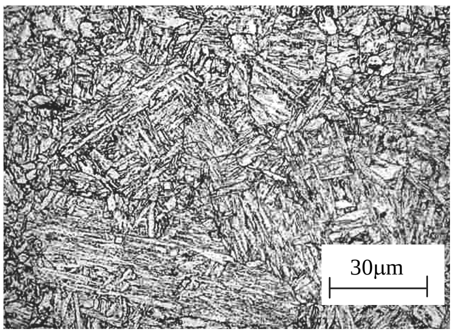

Fig. 18. HCM12A steel microstructure after 30 thousand hours of operation. LM

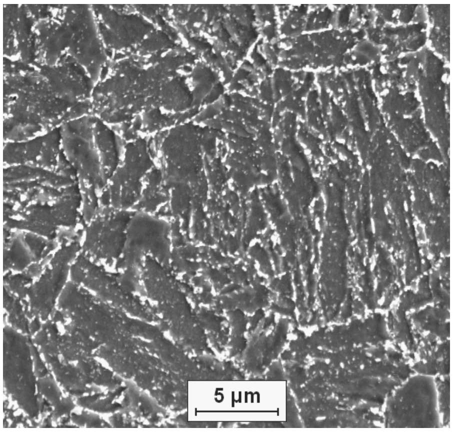

Fig. 19. HCM12 steel microstructure after 30 thousand hours of operation. SEM

The substructure investigation of HCM12A steel showed presence of $M_{23}C_6$ and MX carbides (Figs. 20, 21) and Leves phases as well (Figs. 22, 23). The morphology of Laves phases after longer time of exploitation is was more irregular than in comparison to $M_{23}C_6$ carbides. Moreover they were observed mainly on grain boundary and near of $M_{23}C_6$ carbides. There was found effects of recovery process such as in the case of HCM12 type steel (Fig. 24).

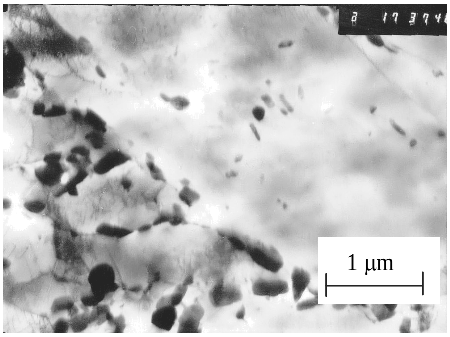

Fig. 20. The substructure of HCM12A steel with M23C6 and MX carbides

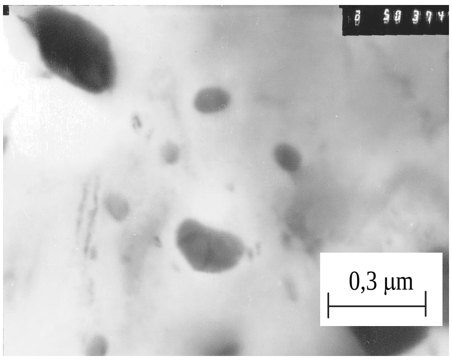

Fig. 21 a. The substructure of HCM12A steel with $M_{23}C_6$ and MX carbides. Details from Fig. 20

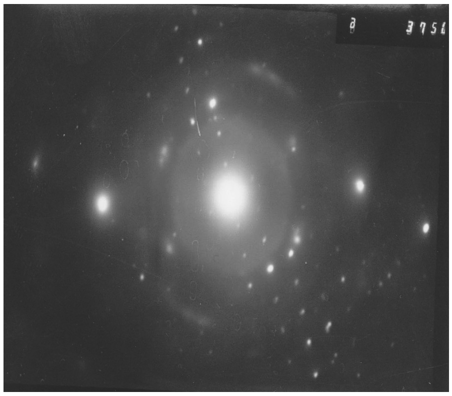

Fig. 21 b. The substructure of HCM12A steel with $M_{23}C_6$ and MX carbides. Details from Fig. 20

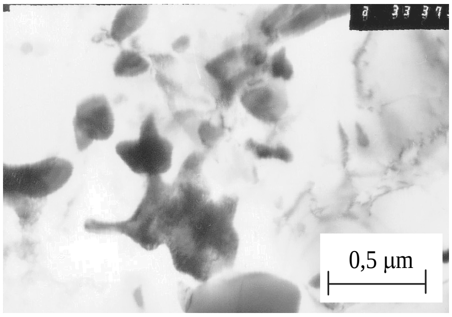

Fig. 22. The substructure of HCM12A steel with Laves phases

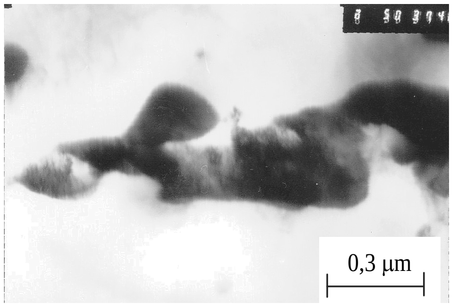

Fig. 23. The substructure of HCM12A steel with Laves phases. Details from Fig. 22

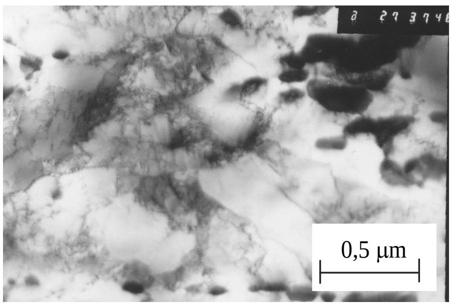

Fig. 24. The recovery processes in the matrix of HCM12A steel after 30^{th} hours of operation

2.2. Mechanical properties

The results of mechanical examinations at ambient temperature and at a temperature of 600ºC are shown in Table 2, and in Table 3. The investigated specimens was made from steam superheater tubes made of HCM12 and HCM12A steel grades, with 38 mm diameter and wall thickness 4, 6.3 mm respectively.

Table 2.
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 3.
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 structural investigations of HCM12 power plant steel showed that after 20000 h of exposure in operation condition, the microstructure of this steel consist two major types of elements such as tempered martensite and δ̃–ferrite in the amount of up to 30%> There was found the carbide precipitations mainly located along ferrite grain boundaries and partially inside the grain. During process of long term exploitation in actually conditions at high temperature a thermally activated processes of recovery and polygonization was observed. In this conditions the intensity of carbides precipitation was place as well. This precipitations process was related to generation mainly of $M_{23}C_6$ carbides, uniformly distributed throughout primary austenite grain boundaries and throughout martensite laths. There was found fine-dispersion precipitations of VC and acicular precipitations of $M_{23}C_6$ in areas of d-ferrite as well. The microstructural investigations of this steel after next 10000 h of exposition showed a typical of this steel grade two-phase structure of tempered martensite with δ̃–ferrite. In comparison to shorter time of exposure a considerable fraction of carbide precipitations inside the grain was observed. The hardness level of this material after 20000 h is 208 HV. After 30000 hours of operation this steel shows a hardness level higher than the required minimal value of 200 HV – 211 – 214 HV. The mechanical properties fulfill the requirements of relevant standards as well, i.e. the yield point at a room temperature is higher than 390 MPa; the yield point at 600ºC is higher than 250 MPa and the elongation is lower than the minimum 20%.

The same type of investigations used to description microstructural changes in HCM12A steel shows that in this case a structure consist the same like in HCM12 steel a tempered martensite but with much smallest fraction of δ–ferrite (<5%). Similarly like in the earlier case the precipitations of $M_{23}C_6$ carbides were observed on grain boundaries. TEM investigations showed presence of well-shaped polygonal subgrains, where low dislocation density was observed. Precipitation of longitudinal and coagulated shapes of $M_{23}C_6$ carbides was presented mainly on equiaxial subgrain boundaries. Moreover the MX precipitations were onserved inside the subgrains.

The examinations of structure after next 10000 hours of operation this steel shows a slight changes in micro and substructure. The microstructure is still typical for this type of steel grade and consist a tempered martensite with an insignificant amount of δ–ferrite and a small amount of carbide precipitations inside the grain.

The hardness measurement showed that after 20000 h of exposition this value was 223 HV. After next 10000 h a hardness was at a level higher than the required minimum value of the order of 200 HV, i.e. 214-220 HV. The others 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% [19].

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. 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 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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