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Development of the precipitation processes in low-alloy Cr-Mo type steel for evolution of the material state after exceeding the assessed lifetime

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Materials

ABSTRACT

Purpose: of this paper is to present the changes of the structure and of the carbides composition in material components made of 13CrMo44 after long term service in creep conditions.
Design/methodology/approach: The material of the research studies has been obtained from Polish power stations. All examined elements have exceeded their assessed life of 100,000 hours. The microstructures of the elements have been observed using a scanning electron microscope. The mechanical properties and hardness values have been obtained. X-ray diffraction has been used for identification of carbides. The Rietveld method has been applied to calculate factions of the carbides.
Findings: The correlation between changes in the carbides' composition and equivalent service time and exhaustion extent has been presented.
Practical implications: The presented method can be used for evaluation and qualification of structural changes in power station boiler components operating in creep conditions.
Originality/value: The application of the Rietveld method for quantification of the carbides for evaluation of the state of the material being in operating conditions.
Keywords: Metallic alloys; Phase analysis; Rietveld method; SIROQUANT ^{TM}

1. Introduction

Not so many recently built units have been noted in the Polish power industry during the last dozen years at least. Therefore, producers of the electric energy aim their main efforts to maintaining the availability of the existing units, securing simultaneously their safe operation. Carrying out their overhauls and repairs is the correct way to attain these goals. However, overhauls and repairs call for the dependable and rational diagnostics to be carried out. Modernization of the units in service is necessary also apart from the overhauls and repairs to maintain in Poland the present electric energy and heat production level [9-15].

Therefore, the essential problem to solve is the assessment of the power boiler pressure part state and forecast of its further safe service. Evaluation of materials of the elements in creep service features one of the main elements within the framework of such assessment. The system developed in the Institute for Ferrous Metallurgy for evaluation of the material condition after the long-term service in these conditions calls for carrying out the assessment of changes occurring in structure [1-4]. Evaluation of structure changes may be carried out based on the microstructure image in the area of changes occurring in its phase constituents, development of internal damages, and changes occurring in the carbides' precipitation processes. The non-destructive examination methods were developed for evaluation of these changes that may be used directly on the industrial objects. This work presents a fragment of research in the area of assessment of the development of precipitation processes due to the long-termcreep service. Occurrences of the particular carbide types is connected with the degradation extent of the material. Their qualitative phase analysis makes identification possible of carbides isolated from the steel and evaluation of their proportions [6]. However, this analysis is not sufficient to determine their true proportions. Getting not only the qualitative, but also the quantitative images of the precipitation development processes provides the possibility of the accurate assessment of the material exhaustion extent. Rietveld metod has made the quantitative phase analysis possible. This method was previously used for the quantitative phase analysis of the carbide isolates in the IF type steels [7].

The goal of this work was to reveal relationships between changes occurring in the phase system pf carbides precipitations, equivalent service time and the exhaustion extent in reference to the mechanical properties and hardness.

2. Material for investigation

The 1Cr-0.5Mo type low-alloy steel with the ferritic-pearlitic structure was the material for investigation, being used for the pressure part elements of the power boilers. The required chemical composition of the investigated steel is presented in Table 1a. Elements made from this steel, in service at the most demanding thermal and stress conditions, are the steam superheater coils, as well as their sections in areas of the inlet to the thrust chamber of these superheaters. The material structure changes occur quickest in these elements and getting sections for the distructive testing does not pose any significant problems. From among many sections taken for examinations some were selected, whose structure state and the precipitation development processes extent ensured the expected structure of the on-going changes. Service parameters and elements types, from which sections were taken are listed in Table 1b.

3. Equivalent service time

The notions of the equivalent service time t_{ew} and the equivalent temperature T_{ew} were introduced to ensure the comparative analysis of materials in service at various parameters [6]:

$T(C+\log t_e)=T_{ew}(C+\log t_{ew})$, $t_{ew}=10^{Te/T(C+\log t\ ew)-C}$

where: C- material constant, t_e – service time, T_e – service temperature, T_{ew} – assumed equivalent temperature.

Based on the known total thickness of oxides on the inner side of the examined sections of boiler pipes and known real service time, the equivalent service temperature T_e was evaluated. Next, the equivalent service time $t_{ew\ 540°C}$ was evaluated for the equivalent service temperature T_{ew} = 540°C [1,3,5]. Calculation results are presented in Table 2.

4. Effect of the long-term service on mechanical properties and structure

Mechanical properties tests for materials with the various values of the equivalent service time $t_{ew\ 540}$ did not reveal any correlation with the development of the precipitation processes. However, their notable decrease was revealed for the material with the significant degradation extent. An example of this lack of correlation are the yield point test results at the temperature of 500°C depending on time $t_{ew\ 540°C}$ shown in Fig. 1. However, the HV10 hardness (Table 2, column 2) decreased notably along with the increase of the equivalent service time $t_{ew\ 540°C.}$ Corresponding to it are the particular structure degradation level and change of the types and amount of carbides (Table 2, column 3). Examination of the material's microstructure was carried out on the transverse sections and its observations on the scanning electron microscope were made at magnifications of up to 3000x. Test results are presented in Table 3. Assessment of the material state was carried out based on the own material structure templates in the initial state and after its long term creep service as well as using the own classification of the Institute for Ferrous Metallurgy, depending on:decay extent of the main structure phases, development level of the precipitation processes, exhaustion extent, and hardness test results [2, 5].

The material states of the examined coils sections were assessed based on these results and their exhaustion extent was evaluated. Results of this assessment are presented in column 3 of Table 3.

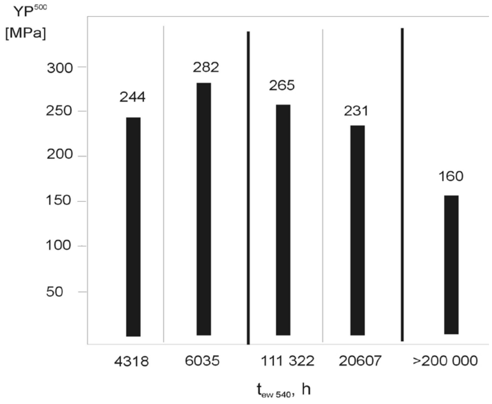

Fig. 1. Dependence of the yield point at temperature of 500°C on the equivalent service time $t_{ew\ 540°C}$ of the 1Cr-0.5Mo low-alloy steel after long-term creep service

5. Effect of the long-term service on carbides precipitation processes development

Development of the carbides precipitation development processes may be evaluated based on the structure image by analysing their sizes, shapes, locations, and estimating the amount of carbides.

Such estimation was made in column 3 of Table 3: material state – precipitations. However, it is the qualitative assessment only which is not always sufficient. Therefore, idenitifcation of the precipitations is carried out, as well as the semi-quantitative assessment, as far as their amount is concerned, using the X-ray diffraction of the carbides isolate.

One can make such assessment knowing the sequence of precipitations for the investigated material from its initial state to the state being characteristic for structure degradation, for which ferrite with carbides is the charactersitsic image. However, a more precise state assessment is possible only when the quantitative assessment is possible. The quantitative assessment was done using Rietveld's method for the X-ray phase analysis. Examinations were made using the X-ray diffractometer using X-ray diffraction after isolating the precipitations and determining the mass of the investigated carbide isolates.

Table 1.
Material for investigation
a) chemical composition of the investigated steel according to PN-85/H-84024

PN-75/H-84024	Chemical composition [%]									
	C	Mn	Si	P	S	Cr	Ni	Mo	Cu	Al
	0.11-0.18	0.40-0.70	0.15-0.35	max. 0.04	max. 0.04	0.7-1.0	max. 0.35	0.4-0.55	max. 0.25	max. 0,02

b) service parameters and types of the investigated elements

No	Service time [h]	Service parameters		Element type – Dimensions [mm]
		Design pressure p_o [MPa]	Design temperature T_o [°C]	
1	69 618	16,18	510	live steam superheater coil - ϕ 44.5x4
2	91 979	6,0	550	live steam superheater coil - ϕ 51x4
3	148 054	6,0	550	live steam superheater coil - ϕ 51x4
4	148 054	6,0	550	live steam superheater coil - ϕ 51x4
5	122 621	6,0	550	live steam superheater coil - ϕ 51x4

Table 2.
Evaluation of the equivalent service time $t_{ew\ 540°C}$ for the constant equivalent service temperature T_{ew} = 540°C

No	Service time t_s[h]	Total thickness of the oxides layer Δ_g [μm]	Equivalent service temperature evaluated based on deposits' thickness T_e [°C].	Service time t_{ew} for the equivalent temperature T_{ew} = 540°C
1	69 618	53.1	510	4 318
2	91 979	63.0	511	6 035
3	148 054	98.0	522	20 607
4	148 054	125.0	536	111 322
5	122 621	257.0	588	>200 000

Cobalt radiation was used with monochromatization of the beam diffracted on the graphite monochromator. Qualitative analysis of the carbide precipitations was carried out based on the standard roentgenographic data from the ICDD database in PDF-4 2005 version. SIROQUANTTM program was used to carry out the quantitative phase analysis. The detailed presentation of the employed investigation methodology and investigation results will be published separately. Results of the qualitative and quantitative phase analyses of carbides in isolates obtained from the material of the investigated elements from the 1Cr-0.5Mo steel after varying service time at different temperatures in similar stress conditions are shown in histogram form in Fig. 2

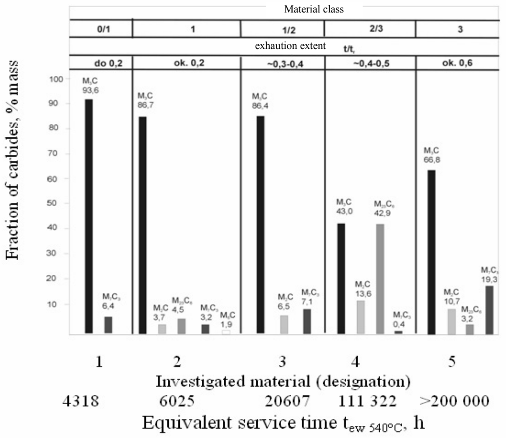

Fig. 2. Changes of the carbides types and their quantitative fractions versus the growing equivalent service time $t_{ew\ 540°C}$ at the progressing structure degradation process of the 1Cr-0.5Mo low-alloy steel after long-term creep

Analysis of occurrences of the particular types of precipitations and their amounts, depending on the equivalent service time and exhaustion extent defined as the ratio of service time to the time of material's damage, has confirmed the correctness of the sequence assumed so far of occurrences of the particular types of carbides at the different stages of material degradation in creep service [8].

6. Conclusions

1. No clear correlation between the mechanical properties test results and development of the precipitation processes and exhaustion coefficient was found, albeit these properties deteriorated notably for the material with the significant structure degradation extent.
2. Hardness of the investigated material decreases with service time. The particular structure degradation level and change of types and amount of the carbides correspond to the this hardness.
3. The direct correlation was found between the structure image analysis in the area of the carbides precipitation processes development and the qualitative assessment of the occurring carbides types and the quantitative one of their fractions in respect to the exhaustion extent.
4. The calculated fractions of the carbides types change versus the equivalent service time. A clear decrease of the M_3C cementite amount is observed, and after exceeding the service time of 100,000 hours the brief increase of the $M_{23}C_6$ carbide amount growth takes place, which decreases later. The M_7C_3 carbide develops often then, which is metastable and transforms into the M_6C carbide most often, whose amount grows notably after the long-term service.
5. The sequence of occurrences of the particular carbides types assumed so far, depending on the material degradation level and development of the precipitation processes in creep conditions, noted in short:

Table 3.
Microstructure investigation results on the scanning electron microscope of the 1Cr-0.5Mo type low-alloy steel after the long-term creep service

No	Equivalent service time $t_{ew\ 540°C}$ Hardness HV10	Microstructure description Material state – exhaustion extent [1.)]
1	2	3
1	4318 156	Ferritic-pearlitic structure with with some bainite. The pearlite-bainite areas with the shape not varying from the chcracteristic one for the initial state of the investigated steel. No discontinuiities nor micro-cracks were observed in the structure. Pearlite/bainite areas: class 0/I, precipitations: class o/a; Structure discontinuities class O CLASS 0/1, DEGRADATION EXTENT: up to 0.2
2	6035 159	Ferritic-pearlitic structure. Pearlitic areas slightly coagulated with the retained lamellar cementite structure. Numerous, rather fine, chained precipitations on ferrite grains boundaries. No origination of damage processes observed. No discontinuiities nor micro-cracks were observed in the structure. Pearlitic areas: class 0/I, precipitations: class a; Damage processes class O CLASS 1, DEGRADATION EXTENT: ~ 0.2
3	20607 151	Ferritic-pearlitic structure. Partially coagulated pearlitic areas. Numerous, fine, chained locally precipitations on ferrite grains boundaries. Quite numerous rather evenly distributed fine precipitations inside ferrite grains.No origination of damage processes observed.No discontinuiities nor micro-cracks were observed in the structure. Pearlitic areas: class I, precipitations: class a; Damage processes class O CLASS 1/2, DEGRADATION EXTENT: ~ 0.3
4	111322 128	Ferritic-pearlitic structure. Pearlitic areas significantly coagulated, locally only visible strongly fragmented cementite plates. Precipitations on ferrite grains, some of them rather big. No origination of damage processes observed. No discontinuiities nor micro-cracks were observed in the structure. Pearlitic areas: class I/II, precipitations: class a/b; Damage processes class O CLASS 2/3, DEGRADATION EXTENT: ~ 0.4÷0.5
5	> 200000 126	Ferritic-pearlitic structure. Pearlitic areas significantly coagulated, locally only visible strongly fragmented cementite plates. Precipitations on ferrite grains, some of them rather big. No origination of damage processes observed. No discontinuiities nor micro-cracks were observed in the structure. Pearlitic areas: class I/II, precipitations: class b; Damage processes class O CLASS 3, DEGRADATION EXTENT: ~ 0.5

Note: 1.) According to the own classification of Institute for Ferrous Metallurgy [1, 6]

$$M_3C \rightarrow M_2C \rightarrow M_{23}C_6 \rightarrow M_7C_3 \rightarrow M_6C$$

has been confirmed with the obtained results of the qualitative and quantitative X-ray phase analyses.

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