The identification of carbide phases by XRD analysis as the method of assess the extent of the steel damage after long time in service

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Abstract

After long time in service in contact in a superheated steam mechanical properties of materials decrease. Experiments revealed that the XRD analysis of electrocemically separated carbide phase is a rapid and informative method of evaluation the service condition of steel. Mechanical properties of ferritic and bainitic low-alloy steels are caused by many factors like: chemical composition, quantity and the kind of microstructural constituent, the precipitation hardening, substructure of matrix and index of matrix lattice defects. In this paper the results of investigations 13CrMo4-5 steel was shown. The material for research was taken from thermal power plant elements. Material A was after 150.000 hours of work as the pressure chamber in which was the temperature 530-580oC and the pressure was 12 MPa. Material B was after 250000 hours of work as the pipeline of superheated steam. The temperature in this case was 530oC but the pressure was 12 MPa as well. The mechanical properties after long time service and changes in fine structure were tested. Parameters of carbide phase electrochemical separation in electrolytes solutions are presented in this work.The most relevant electrolyte and the far better conditions of extraction process were chosen taking into consideration the time needed to get considerable amount of carbide phase constituents. The identification of carbide phases was the special goal of this work. Identification of electrochemically separated carbide phases by means of the XRD analysis was used.

Keywords: carbide phases, evaluation the service condition of steel, XRD analysis, low-alloy steels, electrochemical separation, mechanical properties

1. Introduction

When bainitic steel are exposed to elevated temperatures during long time in service precipitation of various carbide phases take place. On exposure to elevated temperatures during service carbide phases tends to transform one to another. Relatively minor amounts of carbide phases can have major effect on mechanical properties of those steels. This effect strongly depends of the phase composition between carbide phases. Some of the necessary information about matrix structure and carbide phases can be obtained from microstructural analysis by optical metallography, scanning electron microscopy and electron transsmision microscopy [1]. However, for carbide phases, it is always advantageous to know the phase composition and the quantity of the individual phases . The XRD analysis is the best method for this goal. This method could be effective only by separating the phases and consolidating them free of matrix contamination. The essential principle of separation of the phases is based on the selective dissolution of the matrix under appropriate conditions. Between many electrolytes use to the electrochemical anodic dissolution technique only a few can be quantitative for the separation of all kind carbide phases which could to precipitate in low alloy bainitic steels.

In this paper the results of XRD analysis of the extracted by electrolytic anodic dissolution carbides residues and their influence on mechanical properties are described.

2. Experimental procedure and results

2.1. Chemical composition

For research two compositions of low-alloy steels were used. The Table 1. contains chemical compositions of these steels obtained using spectroscopic analysis method

Table 1.
Composition of steels used

	Composition (wt %)								
	C	Mn	Si	P	S	Ni	Cr	Cu	Mo
A	0,153	0,601	0,230	0,018	0,031	0,080	0,981	0,09	0,411
B	0,169	0,426	0,189	0,013	0,020	0,097	0,437	0,21	0,975

2.2. Mechanical properties

Investigations of mechanical properties contain tensile testing at ambient temperature, impact strength and notch sensitivity. Results of mechanical properties after exploitation have been shown in the Table 2 where the average value is $\bar{x}$ and standard deviation S(x).

The sampling place of impact tests tensile bars, V-notch Charpy specimens end notch impact toughness test specimens was settled as shown in Figure 1. For tension impact tests tensile bars of a circle of 5 millimeters in diameter were used. For each test point five specimens were tested. Measuring capacity of the testing machine was 0÷40000 N with the constant operating speed of 200 N/s. The Figure 2 shows tensile strength R_m and yield point R_e.
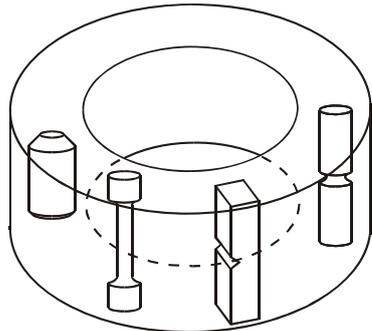

Fig. 1. Schematic illustration of the sampling place of specimens

Because of both steels plasticity for crack resistance testing test method of fracture toughness by measurement critic value J integral, J_{IC} was applied.
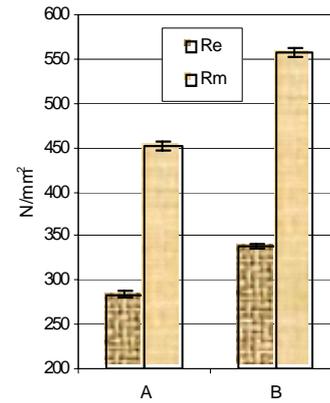

Fig. 2. Mechanical properties after exploitation

Table 2.
Tensile properties, ductility and hardness

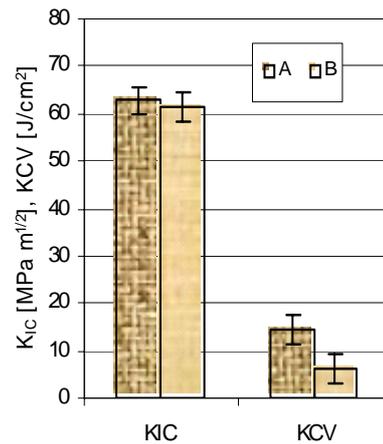|		A	B
Re [MPa]	$\bar{x}$	287	340
	S(x)	4	5
Rm [MPa]	$\bar{x}$	450	551
	S(x)	3	7
A [%]	$\bar{x}$	27,6	24,3
	S(x)	1,2	1,2
Z [%]	$\bar{x}$	52,5	57,9
	S(x)	1,6	0,6
HB	$\bar{x}$	146	175
	S(x)	2,1	1,0
KCV [J/cm^2]	$\bar{x}$	14,1	6,15
	S(x)	1,5	0,3
J_{IC} [J/mm]	$\bar{x}$	19,5	18,6
	S(x)	1,1	0,2
K_{IC} [MPa·m$^{1/2}$]		63,1	61,5

Fig. 3. Impact strength and notch sensitivity after exploitation

The low overall dimensions of testing materials were the reason for which the ASPEF (Absorbent Specific Energy Till Fracture) [6] method was used.

The stress intensity factor K_{IC} was calculated as the value of the fracture toughness.

$$K_{IC}{}^2 = J \cdot E$$

where:
J – critic value integral
E - Young's modulu

The notch impact toughness test was made using longitude Charpy V specimens with the notch radius of 0,25 millimeters. For each test point five specimens were tested. The pendulum impact testing machine with 150 J energy was applied. The Figure 3 shows results of impact intensity factor K_{IC}.

2.3. Microstructural characterization

The microstructure of the materials was studied as function of exploitation time using optical, transmission and scanning transmission electron microscopy. The microstructure of the Cr-Mo low-alloy steels consists of ferrite and bainite with a different dislocation density and finely distributed carbides. For the application of these materials in steam power plants, the micro structural stability during service is of great importance. The following structural features can exert an influence on mechanical properties of the steels:
➢ the precipitation and transformations of carbides
➢ uniformity of the dispersion of carbides
➢ changes of the carbides morphology
➢ the disintegration ferrite/bainite regions
➢ the decrease in the level of Cr and Mo contains in the steels matrix
➢ the decrease in grain boundaries areas of precipitates.

Fig. 4. Optical photomicrograph of ferrite and bainite in the A steel, after etching 5% HNO3, 200x
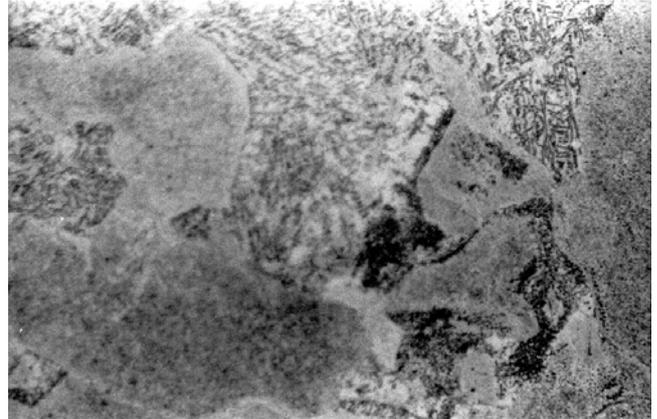

Fig. 5. Optical photomicrograph of ferrite and bainite in the B steel, after etching 5% HNO3, 500x
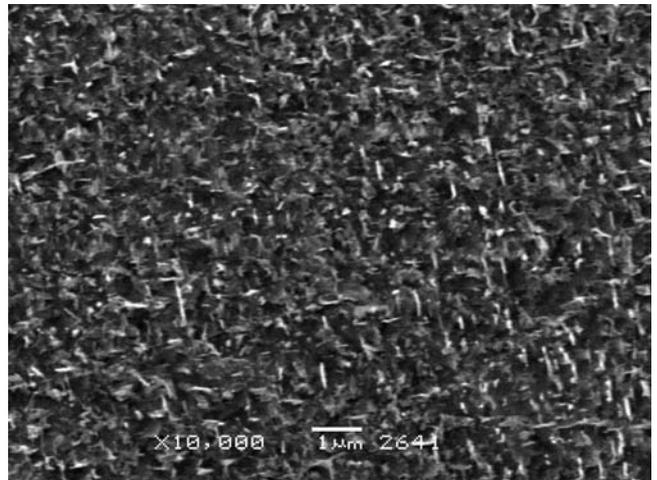

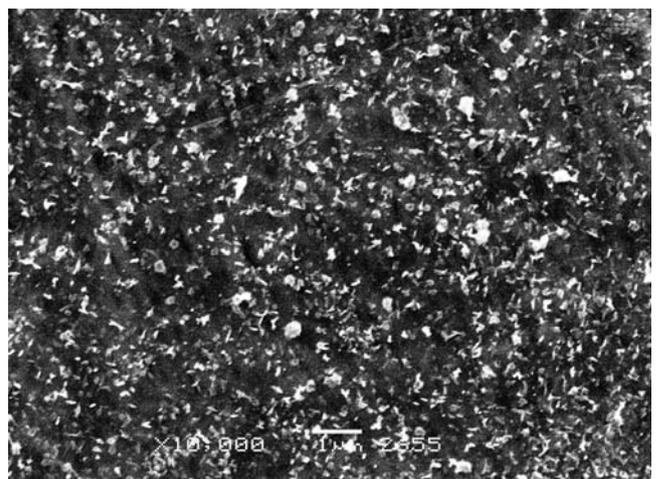Fig. 6. SEM micrograph of A steel showing the ferrite region with carbide precipitation

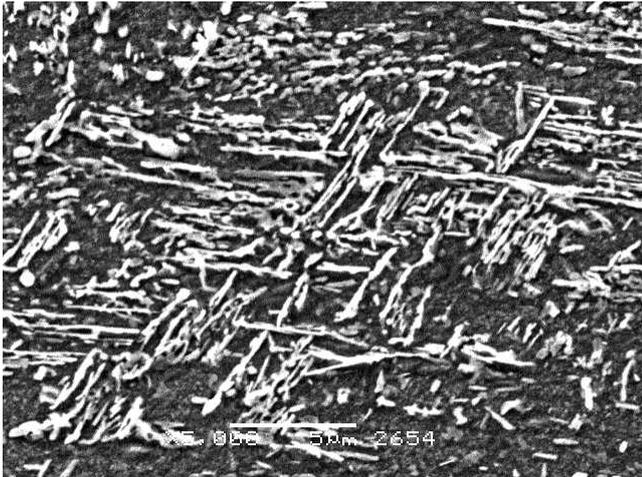Fig. 7. SEM micrograph of B steel showing the ferrite region with carbide precpitation

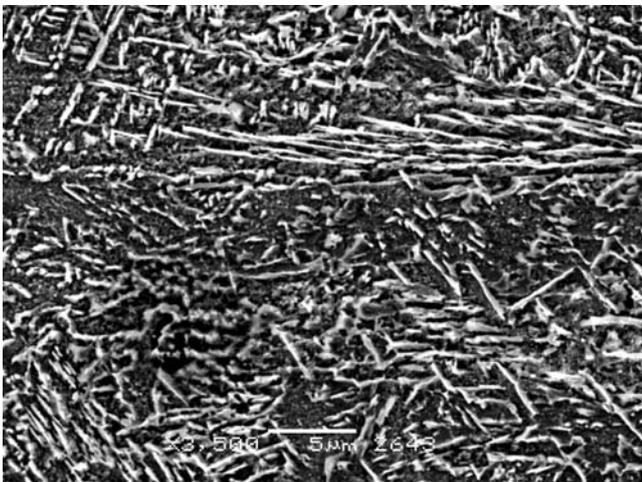Fig. 8. SEM micrograph of A steel showing the bainite region

Fig. 9. SEM micrograph of the bainite region in B steel

Fig. 10. Optical photomicrograph showing spaces without precipitation in A material, after etching 5 % HNO$_3$ 500x

Fig. 11. Transmission electron micrograph of the region low dislocation density

Elem	% wag.	% at.
SiK	2	5,8
MoL	82,3	71
CrK	1,6	2,5
MnK	0,4	0,6
FeK	12,6	18,6
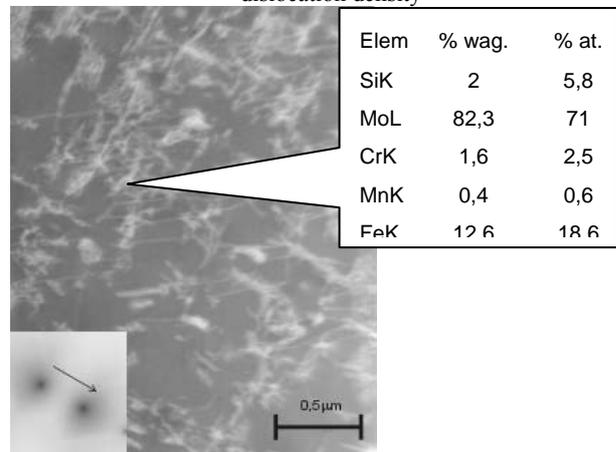
Fig. 12. Transmission electron micrograph of the region with high dislocation density

The identification of ferrite and bainite was made using scanning transmission electron microscopy. Differences in ferrite (Figures 6 and 7) and bainite (Figures 8 and 9) morphology caused by different time of exploitation were observed. In specimens after a longer time of exploitation the progress in coagulation of precipitated phases could be observed (Figures 6 and 7) mainly within ferrite regions. In bainite this process is not as easy to observe because of large numbers of fine dispersed carbides which could be observed in both A and B materials (Figures 8 and 9). Moreover spaces situated close to ferrite grain boundaries about 20 μm wide without precipitations were observed (Figure 10).

In both A and B materials irrespective of whether those longer time were in service during transmission microscopy investigations regions with different dislocation density were observed (Figures 11 and 12). As shown in Figures 11 and 12 with the accompanying diffraction pattern, which was taken from a region of carbide participation molybdenum is the main component of those carbide phase.
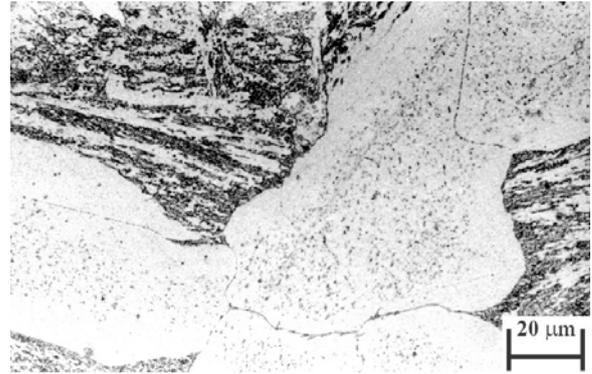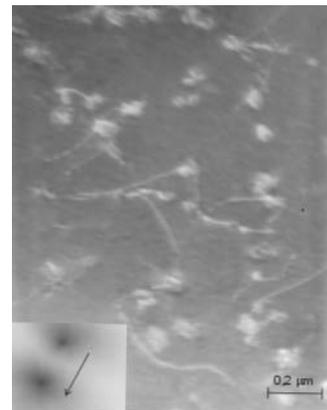
2.4. Electrolytic separation

To indicate the quantitative content of carbide phases the electrochemical isolation was applied. For separating carbide phases from Cr-Mo low-alloy steels many different electrolytes are widely used [2-4, 7-9]. Based on this data published in

literature and using results of previous investigations made by myself before one of those electrolytes and the conditions under which the processes of an electrolytic extraction should be conducted was chosen [12].

The Table 3 contains chemical compositions of the electrolytes proposed by A. Baltusnikas and co.[2]:

Table 3.
Chemical composition of 12H1MF steel electrolyte solutions [2]

no	Chemical compositions of electrolyte
1	0.05% HCl
2	0.05% HCl, 0.01% citric acid
3	0.5% HCl, 0.05% citric acid
4	0.5% HCl, 0.01% oxalic acid
5	0.5% HCl, 0.05% oxalic acid

P. Porański and others proposed few electrolytes for ferritic and ferrito-bainitic steels [13]. But we shoud know that they used this proposed electrolytes for separation non-metallic inclusions especialy oxides. It means that we don't know how they work during contact with carbides. The Table 4 contains chemical compositions of the electrolytes proposed by P.Poranski.

Table 4.
Chemical composition of electrolyte solutions [13]

no	Chemical compositions of electrolyte	pH	Electric current density [A/cm^2]	Observations
1	5% sodium citrate 1,2% KBr 0,6% KJ	7	0,01	Corrosion pits
2	2,5% sodium citrate 1% sodium acetate 2% NaCl 1% KJ	7	0,01	Corrosion pits
3	5% sodium citrate 1% KBr 0,6% KJ 1% hydrazin sulfite	6	0,01	Corrosion pits
4	5% sodium citrate 5% sodium acetate 1,2% KBr 0,8% KJ 0,2% hydrazin sulfite 1% potassium thiocyanate	6	0,01	Plain surface of specimens

Electrolytic extraction was carried out to identify the precipitates in both materials by dissolution of matrix in.2,5% sodium citrare, 1% sodium acetate, 2% sodium chloride, 1% potassium iodide, 0,5% potassium thiocyanate in water at a current intensity of 0,0125 A/cm^2 for a duration of 22,5h [3, 4]. In this medium under the used conditions the Cr-Mo low alloy steel phases like carbides MC, M_2C, M_3C, M_7C, M_7C_3 and $M_{23}C_6$ do not show active-passive behavior. At the potential used for extracting carbide phases from ferrite matrix only ferrite dissolve at a finite rate, whereas carbides does not dissolve actively as it remains on the specimen's surface. During this process the specimen is a positive electrode.

2.5. X-ray analysis

The identification of the precipitates prepared by electrolytic extraction was conducted using X-ray diffraction [5]. XRD analyses of the extracted carbide residues were undertaken on a TUR M-62 X-ray diffractometer with continuously rotating specimen stage using Co Kα radiation with wavelength λ = 0,17021nm. Scanning angle 2Θ was between 25 to 130 degrees with a step size of 0,05°. A large rang scanning angle 2Θ was taken for checking participation in an obtaining isolate also other phases. Diffraction patterns were recorded at 30kV and 25mA in five seconds by point detector's movement speed. The peaks recorded were identified with those available in PDF-2 data base [11]. For the material A three principal carbide phases were identified, the Mo_2C, Fe_3C, $M_{23}C_6$ (which is mainly composed of chromium) and M_7C_3 type – $(Cr_{2,5}Fe_{4,3}Mo_{0,1})C_3$. This phases main lattice parameters of 0,2381nm, 0,238nm, 0,2049nm and 0,2037 nm accordingly (Figure 13) were taken as an essential for identification but other lattice parameters are in good fitting to the diffraction pattern as well.

For material B the Fe_3C carbide type could not be identified because on the diffraction pattern three of their most important lattice parameters could not be adjusted [2] (Figure 14).

It does not mean that Fe_3C carbide is not present as a participation in material after 250 000 hours at service but probably their quantitative volume is too small and is below quantity sensitivity by XRD analysis. In addition a few weak diffraction peaks attributable to the M_3C were observed. Although various combinations of M are possible in low alloy Cr – Mo steels, the lattice parameters measured here (0,2088nm 0,2270nm) correspond most closely with those of Fe_2MoC. On diffraction patterns diffraction peaks attributable to the MnS were observed as well. It was possible because optical microscopy investigations revealed non metallic inclusions within both A and B materials.
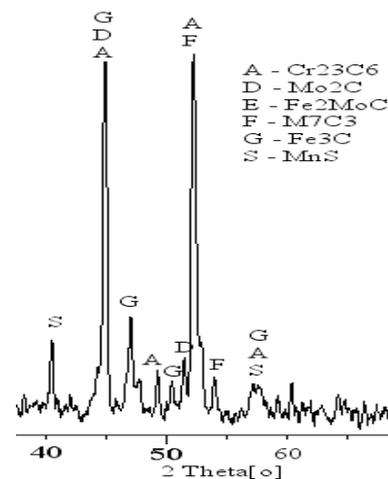

Fig. 13. X- ray diffraction patterns using CoKα radiation (λ=0,17021nm) of carbides extracted from A material
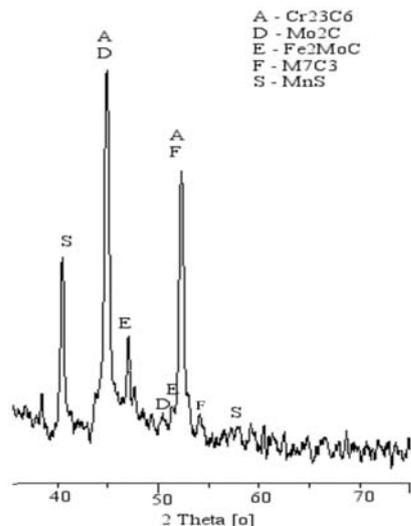
A - Cr23C6
D - Mo2C
E - Fe2MoC
F - M7C3
S - MnS

Fig. 14. X- ray diffraction patterns using CoKα radiation
(λ=0,17021nm) of carbides extracted from B material

2.4. The chemical analysis

The chemical analysis of the precipitates shows the increase
of molybdenum quantity in carbide phases which was measured
after longer time of steel service (Figure 15). This effect was also
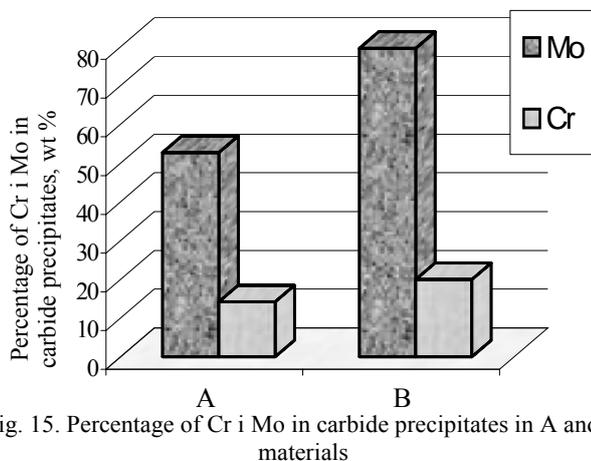observed by Uchara K. and Takano Y. [10]

Fig. 15. Percentage of Cr i Mo in carbide precipitates in A and B
materials

3. Conclusions

The microstructure of the low alloy Cr-Mo steels during long
range service in the thermal power plants pressure vessel elements
undergoes evolution. This evolution causes changes in mechanical
properties.
(1) Changes of the microstructure and progress of carbide phases
precipitation process effect decrease of steels ductility. It was
observed in the impact strength and the fracture toughness as
well.

(2) Changes in other mechanical properties were not observed.
(3) The main reason of decrease ductility was the carbide phases
coagulation and the change in their phase composition caused
mainly by diffusion of molybdenum from matrix to carbide
phases.
(4) Long range service at temperature 550°C causes the Fe$_3$C
carbide to transform to more thermodynamically favored
carbides in which atoms of molybdenum replace atoms of
iron.
(5) Correlation between the mechanical properties for tension
impact tests was observed (mainly tensile strength R$_m$) and
changes in microstructure as also the development of the
precipitation process of carbides.

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