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Evolution of secondary phases in GX12CrMoVNbN9-1 cast steel after heat treatment

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ABSTRACT

Purpose: The paper deals with the investigation of secondary phases evolution during quenching, quenching and tempering in the high – chromium martensitic GX12CrMoVNbN9-1 (GP91) cast steel. It also includes the analysis of evolution of secondary phases in the as - cast condition and after stress relief annealing at the temperature of 750°C of the tempered GP91 cast steel.

Design/methodology/approach: Microstructure of the cast steel was characterized using scanning electron microscopy JOEL JSM 6610LV and high – resolution transmission electron microscopy JOEL JEM - 3010. Identification of the precipitates was made by means of thin foils and extraction carbon replicas. They were analyzed using selected area electron diffraction (SAD). The chemical composition of precipitations was determined by means of energy dispersive X-ray spectroscopy (EDX). Moreover, there were measurements made with regard to mechanical properties (hardness).

Findings: Performed research made it possible to determine the morphology of precipitates for the particular examined conditions of GP91 cast steel. The sequence of precipitation process has been proposed for the investigated cast steel.

Research limitations/implications: It is necessary to continue the research in order to determine the description of microstructure and the type of particles after different heat treatment parameters.

Practical implications: Optimizing the parameters of heat treatment in the aspect of its influence on the morphology of precipitates in GP91 cast steel designed for the power units working under the so-called super-critical parameters.

Originality/value: The relationship between the heat treatment parameters and the type of secondary phases in high - chromium martensitic GX12CrMoVNbN9-1 (GP91) cast steel was specified. Furthermore, the secondary phases in the as-cast condition and after stress relief annealing of the tempered cast steel have been revealed.

Keywords: Metallic alloys; Martensitic 9%Cr cast steel; Precipitates

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PROPERTIES

1. Introduction

Growing demand for electric energy and the limitations on emission of pollutants into the atmosphere, connected with natural environment protection, force the power industry to raise the thermal efficiency of power units. Elevating the efficiency of power units to the expected 50% results in reducing fuel consumption as well as limiting the emission of pollutants to the atmosphere. One of the methods to achieve such efficiency is increasing the steam parameters, i.e. pressure and temperature to the so-called supercritical parameters level. Applying higher parameters of steam entailed the necessity to work out and introduce new materials to the power industry, such as martensitic steels (cast steels) with 9-12%Cr content [1-4], as well as low-alloy bainitic steels 7CrWVMoNb9-6 (P/T23) and 7CrMoVTiB10-10 (P/T24) [3, 5].

One of the cast steels recently introduced in the power industry is GX12CrMoVNbN9-1(GP91) cast steel. It has been developed on the basis of chemical composition of P91 steel and is characterized by higher properties in comparison with the commonly used cast steels, such as: Cr-Mo-V or Cr-Mo. High stability of microstructure of high chromium martensitic cast steel used in the power industry is achieved by heat treatment consisting of hardening (from the austenitizing temperature below 1000°C and quenching - with air or oil) and high - temperature tempering (below 700°C). This kind of heat treatment leads to the formation of microstructure consisting of high tempered martensite and stable precipitates - $M_{23}C_6$ carbides and MX nitrides. Phase transformation or precipitation sequences taking place in the 9% Cr cast steel have not been described. In the cast steel for power industry, both the transformation and the stability of microstructure before and during operation are more important from the practical point of view [4,6-11]. In high-chromium martensitic steels (cast steels) the precipitates are significant factors influencing creep resistance of these materials. Disappearance of precipitates in the microstructure during the service, e.g. MX nitrides in favour of the precipitation of the thermodynamically stable Z phase (Cr(V, Nb)N nitride) leads to a rapid decrease in creep resistance [12,13]. Relatively short and highly general literature data concerning GP91 cast steels is what encouraged the Author to take up the subject matter related to those materials. The main aim of the presented work is to characterize the evolution of the secondary phases in GP91 cast steel after hardening, hardening and tempering and additionally after stress relief annealing of the tempered GP91 cast steel. Moreover, the secondary phases in the as - cast condition of GP91 cast steel have been identified

2. Methodology of research

Chemical composition of the investigated 9% Cr cast steel - GX12CrMoVNbN9-1 (GP91) is shown in Table 1. The GP91 cast steel was heat treated according to the schedule given in Table 2. The last step at 750°C (state No. 5) was given to simulate a Post Weld Heat Treatment (PWHT). The obtained microstructures and their hardness values are included in Table 2 (depending on the applied parameters of heat treatment). Microstructure of the cast steel after heat treatment was classified using JOEL JSM 6610LV scanning electron microscopy (SEM) and JOEL JEM - 3010 high - resolution transmission electron microscope (HRTEM). Particles of secondary phases were extracted in carbon replicas. Moreover, the identification of particles was carried out with the usage of thin foils. They were analyzed using selected area electron diffraction (SAD) and energy dispersive X-ray spectroscopy (EDX). Thin foil for transmission microscopy was prepared by window thinning method using 10%perchlore acid in methanol as electrolyte. Extraction replicas were prepared from well polished and carbon coated specimens using Vilella's reagent. The analysis of the phase equilibrium stability and the numerical simulation of solidification of the examined cast steel was made using the thermodynamic data included in THERMOCALC for Windows (TCW) data bases. Measurement of hardness was taken using the Vickers method with the load of 30kG (294.2 N), by means of the Future - Tech FV - 700 testing machine. For each of the examined state (heat treatment) five measurements of hardness were taken and the received results were averaged and put in Table 2.

Table 1.
Chemical composition of GP91 cast steel, %mass

C	Mn	Si	P	S	Cr	Mo	V	Nb	N
0.12	0.47	0.31	0.014	0.004	8.22	0.90	0.12	0.07	0.04

Table 2.
Schedule of heat treatment

Heat treatment	Heat treatment parameters for GP91 cast steel	Microstructure	Hardness HV30
No. S	as - cast condition	autotempered martensite	232
No. 2	1040°C/12h/water	martensite	486
No. 3	1040°C/12h/oil	autotempered martensite	389
No. 4	1040°C/12h/ oil + 760°C/12h/ air	tempered martensite	201
No. 5	1040°C/12h/ oil + 760°C/12h/ air + 750°C/8h/ furnace	tempered martensite	209

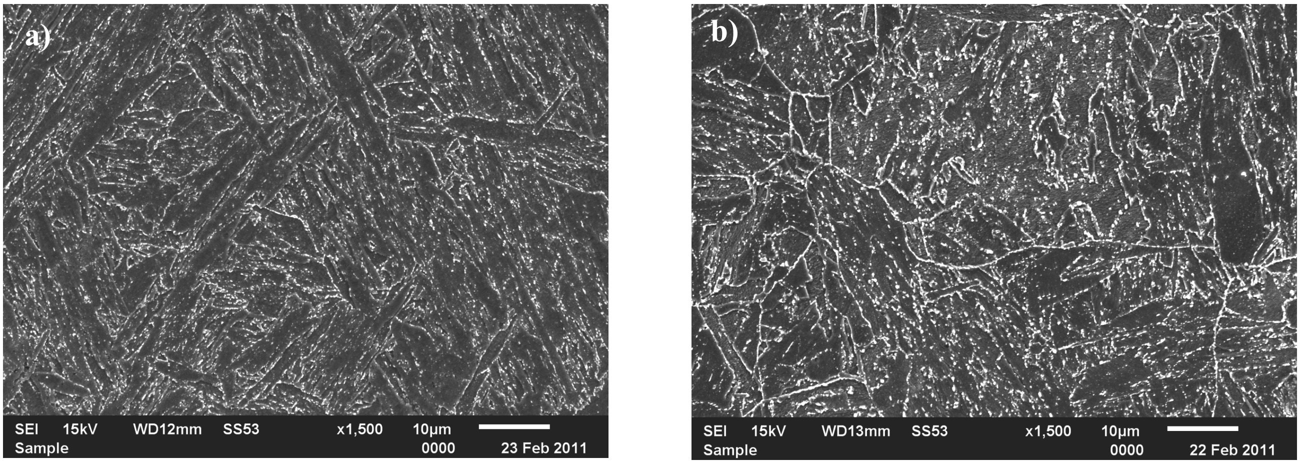

Fig. 1. Microstructure of GP91 cast steel: a) state No. S; b) state No. 5, TEM

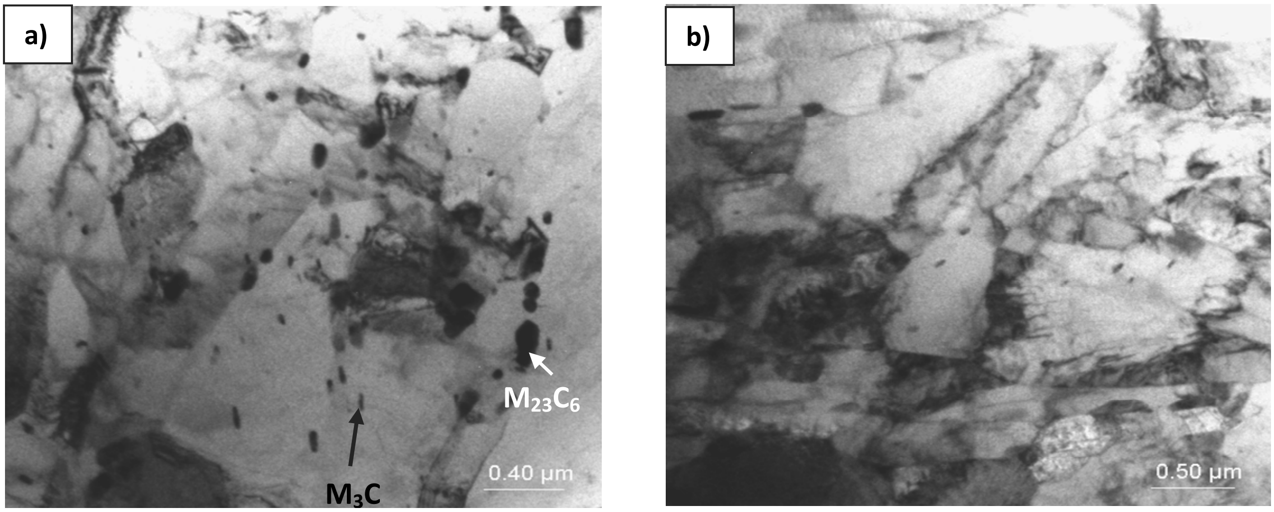

Fig. 2. Microstructure of GP91 cast steel: a) state No. S [9]; b) state No.5, thin foil, TEM

3. Results and discussion

Fig. 1 and Fig. 2 illustrates typical microstructures of the examined cast steel in the as-cast condition (state No. S) and after the heat treatment (state No. 5). Microstructures of GP91 cast steel in state No. S and No. 5 are entirely formed by martensite with large amount of precipitates of diverse morphology. High hardenability of the investigated cast steel, connected with high chromium fraction and additions of molybdenum and vanadium, contributes to the obtainment of martensitic structure regardless of the applied cooling rate. According to [12] the diffusion transformation in P91 steel (whose chemical composition is similar to that of the examined cast steel) takes place at the cooling rate lower than 0.1 K/s.

In the as-cast condition (state No. S) in GP91 cast steel three types of precipitation were observed, i.e. M_3C, $M_{23}C_6$ and NbX. M_3C and $M_{23}C_6$ carbides were precipitated mostly on grain boundaries of former austenite grain and on the boundaries of martensite laths. Single precipitates of this type were noticed inside the laths. Carbides (carbonitrides) of the NbX type were precipitated inside, as well as on the boundaries of subgrains. The NbX precipitates, as revealed in the numerical simulation of solidification of GP91 cast steel which is consistent with the Scheil - Gulliver model (Fig. 3), are precipitated in the final solidification phase. Precipitating thus, the NbX carbides (carbonitrides) act as a factor inhibiting the austenite grain growth, which influences later properties of the cast significantly. According to the data [15] the NbC carbides precipitating in the final phase of solidification may also be the cause of brittleness growth in the cast. An example of morphology and characteristic X - ray spectrum of M_3C and $M_{23}C_6$ carbide is shown in Fig. 4 and Fig. 5. Hardness of the GP91 cast steel in the as-cast condition amounted to 232HV30 (Table 2).

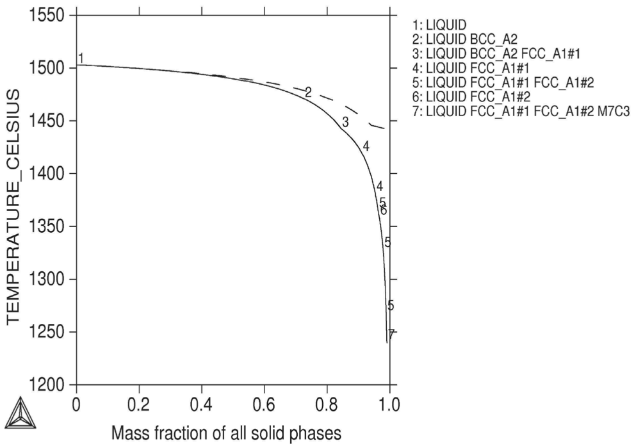

Fig. 3. The course of solidification of the GP91 cast steel determined by means of the ThermoCalc program [14]

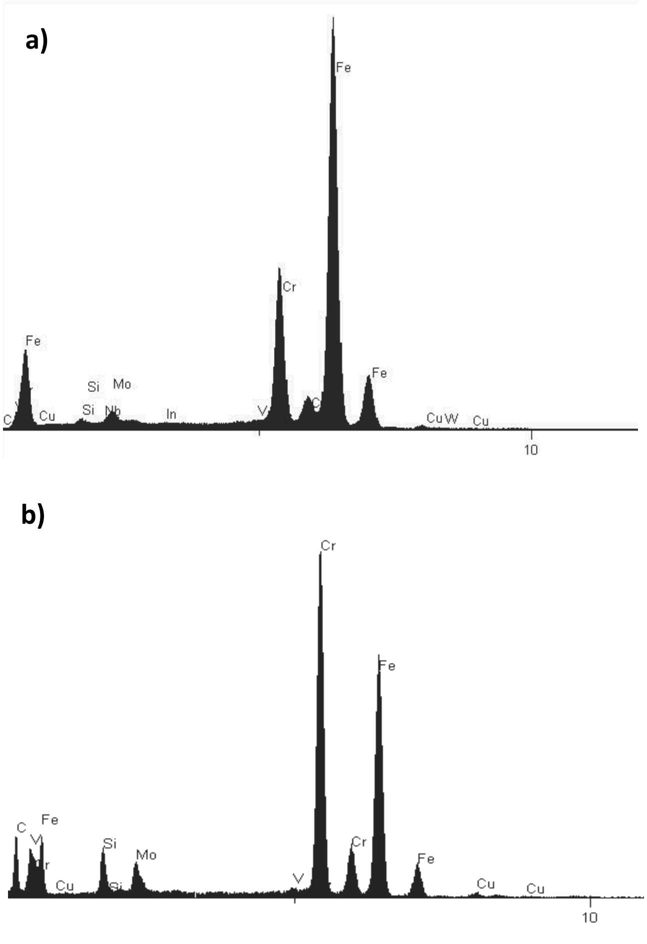

Fig. 4. Typical EDX -a) spectra of M_3C carbide in state No. S; b) spectra of $M_{23}C_6$ carbide in state No. S

After hardening from the austenitizing temperature of 1040°C (state No. 2 and No. 3) the grain boundaries in the examined cast steel were practically precipitate-free. In state No. 2 (after hardening in water) in the microstructure only the fine-dispersion spherical precipitations of NbX were observable (Fig. 6).

In the case of state No. 3, due to a less intense cooling agent - oil, apart from NbX precipitates, the occurrence of equiaxed particles of M_3C was also disclosed (Fig. 6). Both types of precipitates were seen inside the laths of martensite.

The presence of the M_3C carbides in the microstructure of investigated cast steel after hardening in oil (state No. 3) implies dealing with auto-tempered martensite. It is obvious with regard to a relatively high temperature at the beginning of martensitic transformation M_s, amounting to 386°C for the investigated cast steel. The M_s temperature is high enough to allow the carbon diffusion to take place, which results in the precipitation of lamellar (needle-shaped) M_3C carbides inside the laths of martensite. Carbides of M_3C in the examined cast steel are a metastable phase precipitating, according to [16], already after ca. 0.29 s at the temperature of 690°C.

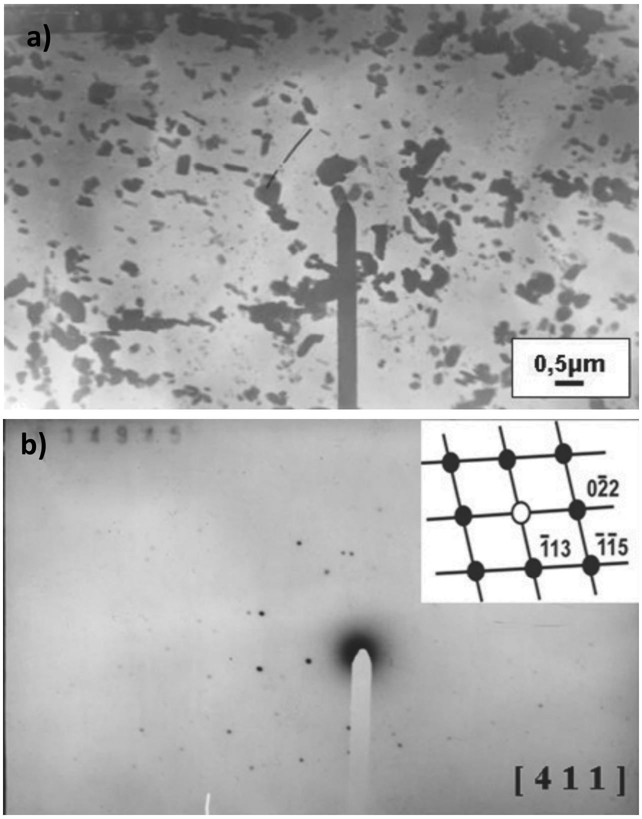

Fig. 5. Intragranular particle of M_3C carbide in state S, TEM, carbon extraction replica; a) morphology of the particle; b) solution of diffraction pattern

Particles of ε - carbide were not found in the microstructure of state No. 3. However, their occurrence in autotempered martensite of 9%Cr steel has been reported by Brühl et al [17] and Soraja et al. [18]. Moreover, in both of the states there were insignificant amounts of retained austenite observed on martensite lath boundaries (Fig. 7). Likewise, lower hardness of the cast steel in State No. 3 (389HV30) in comparison with State No. 2 (486HV30) indicates the process of auto-tempering of martensite in the cast steel hardened in oil.

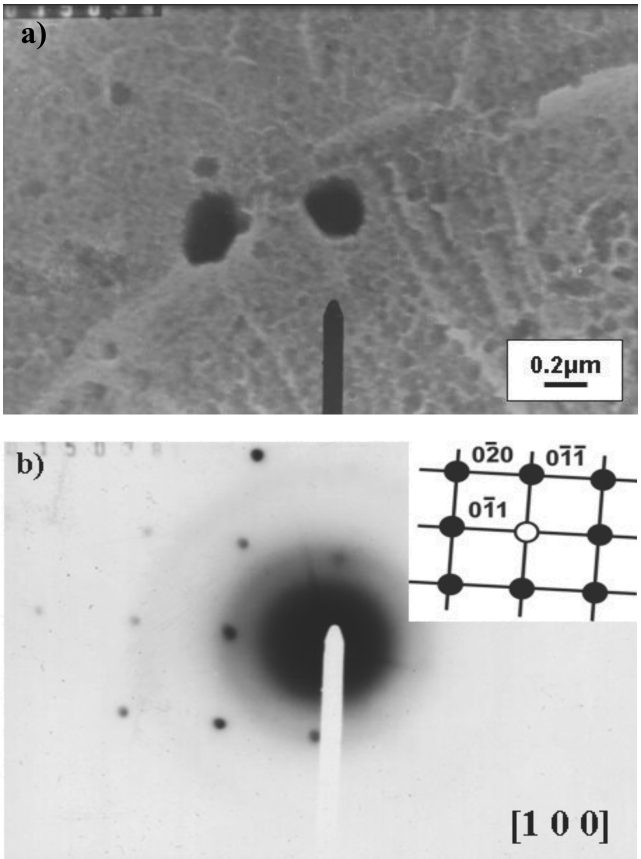

Fig. 6. Intragranular particle of NbC carbide in state No. 2, TEM, carbon extraction replica; a) morphology of the particle; b) solution of diffraction pattern

Performed research has shown that during austenitzing of the examined cast steel at the temperature of 1040°C the solution of precipitates occurring in the matrix is not complete.
What remains after hardening from the austenitizing temperature of 1040°C is some amount of NbX precipitates insoluble in the matrix. As per the TCW software prediction of equilibrium phases in the investigated cast steel (Fig. 8), MX precipitates may be stable even at the austenitizing temperature of 1340K. Similar residual precipitates were also observed by Zielińska [19] and Paul et al. [20].

Microstructure of GP91 cast steel in the state No. 4 shows features similar to the microstructure of state No. 5 of the cast. It consists of $M_{23}C_6$ and MX particles surrounded by high-tempered martensite matrix. Carbides of $M_{23}C_6$ in both of the examined states were precipitated mostly on grain boundaries of former austenite grain and the subgrain boundaries.

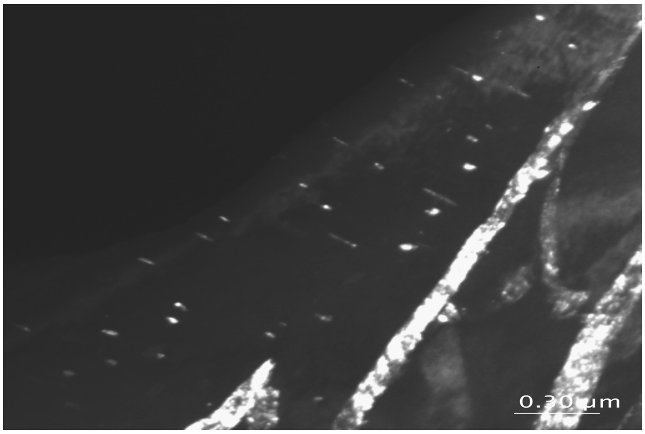

Fig. 7. Lamellar precipitates of M_3C carbides in martensite, state No. 3, thin foil, TEM

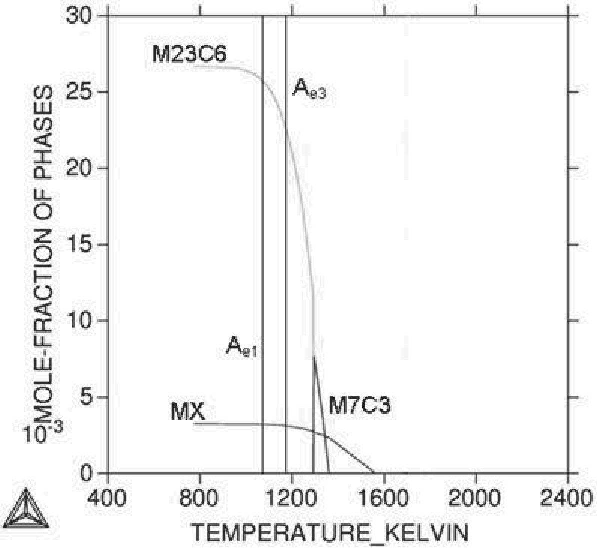

Fig. 8. Influence of the temperature on the mole-fraction of phases calculated by means of ThermoCalc for GP91 cast steel

Former austenite grain boundaries are privileged areas for the precipitation of $M_{23}C_6$ carbides. Carbides precipitating on those boundaries are characterized by larger diameter in comparison with the carbides precipitated on the sub boundaries. Diverse size of $M_{23}C_6$ carbides presumably results from the location of their precipitation. High-angle boundaries of former austenite grain, with their high energy, are the areas of privileged precipitation of secondary phases from the supersaturated solid solution, while the stable boundaries favour the growth of carbides. Example of morphology of $M_{23}C_6$ carbide in state No. 4 is presented in Fig. 9.

According to the calculations presented in work [19], precipitation of $M_{23}C_6$ carbide in P92 steel is finished after ca. 100s at the temperature of 770^{o}C, after ca. 400s at the temperature of 730^{o}C and after ca. 2000s at the temperature of 700^{o}C.

Precipitations of the MX type were mostly revealed inside the boundaries of subgrains, yet on them as well. In the examined cast steel two different morphologies of MX precipitation were noticed, occurring in two forms: as niobium-rich carbonitrides resembling a spherical shape - NbX, as well as lamellar carbonitrides, vanadium-rich nitrides of the VX type (Fig. 10).

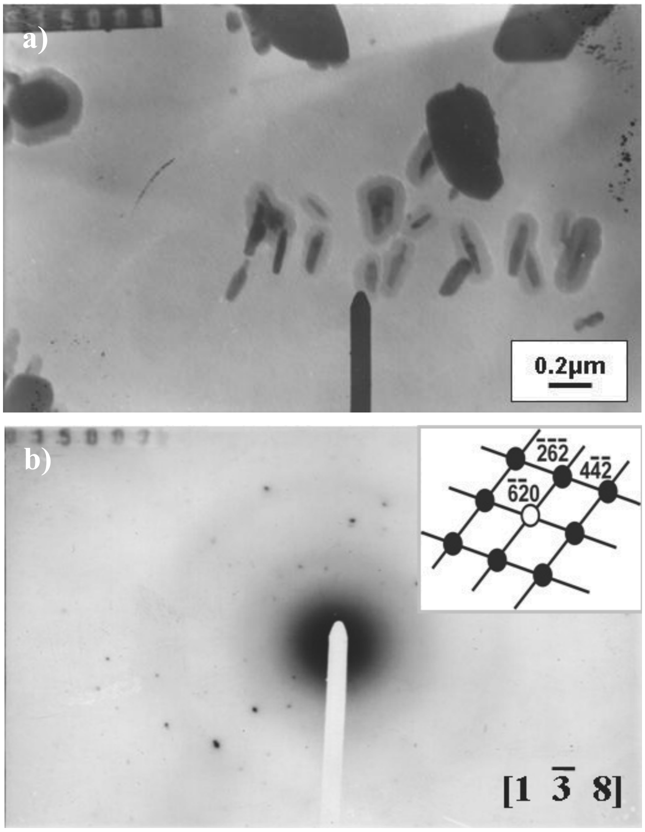

Fig. 9. Particle of $M_{23}C_6$ carbide precipitating at grain boundaries in state No. 4, TEM, carbon extraction replica; a) morphology of the particle; b) solution of diffraction pattern

The V-rich MX particles which were found in the microstructure after tempering evidently precipitate during tempering. It follows that the fine-dispersion precipitates of MX rich in vanadium cause the precipitation strengthening in the investigated cast steel, while the role of MX precipitates rich in niobium is in fact limited to hindering the grain growth during austenitizing.

The $M_{23}C_6$ carbides precipitated in the boundaries of subgrains/laths of martensite play a significant part - stabilizing the subgrain microstructure of martensite and hindering the movement of dislocation boundaries.

Fine-dispersion precipitates of the MX type, precipitated mostly on the dislocations inside martensite laths, anchor and hinder the dislocation movement and provide high creep resistance.

After quenching and tempering GP91 cast steel is characterized by a microstructure typical for 9 - 12%Cr steel, i.e. consisting of ferritic matrix and numerous carbides of $M_{23}C_6$ as well as the MX precipitates diverse in terms of morphology and chemical composition (spherical precipitates rich in niobium - NbX and lamellar precipitates rich in vanadium - VX) - Fig. 6 and 10. Particles of M_2X and M_7C_3 were not identified in the investigated cast steel neither after tempering nor after tempering and annealing. In the 9-12%Cr steels/cast steels the precipitates of M_2X and M_7C_3 are the intermediate phases which are precipitating during tempering at the temperature below 700^{o}C [19,21,22].

The hardness values for GP91 cast steel after the heat treatment - state No. 4 and No. 5 - were similar and amounted to 201HV30 and 209HV30, respectively (Table 2). Similar hardness of GX12CrMoVNbN9-1 (GP91) cast steel after the performed heat treatment, state No.4 and No. 5, indicates high stability of the microstructure of the examined cast steel.

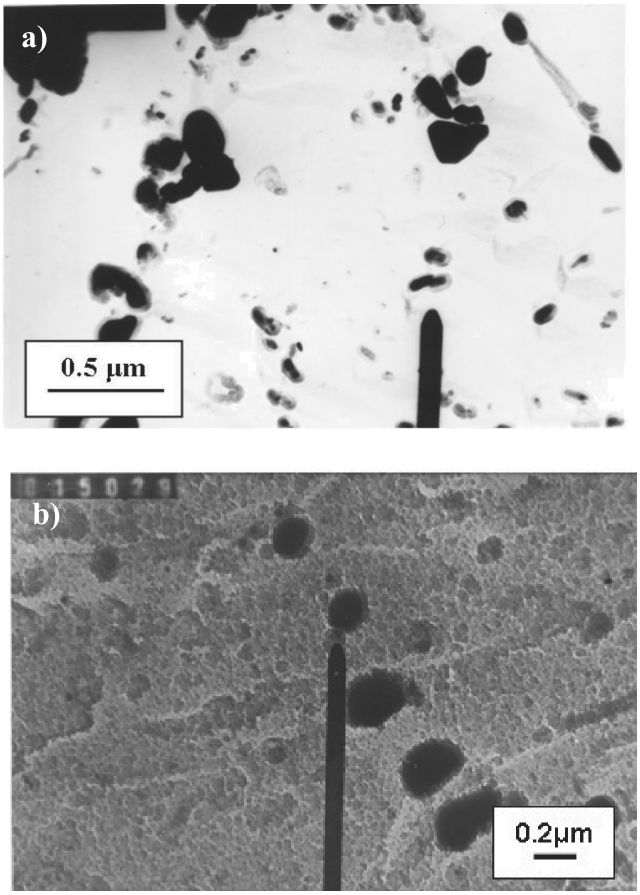

Fig. 10. Precipitations of the MX type in state No. 4, TEM, carbon extraction replica; a) Morphology of the VX particle; b) Morphology of the NbX particle

4. Conclusions

The investigation of secondary phases evaluation of 9%Cr cast steel austenitized at 1040°C and subsequently tempered at 760°C and additionally annealed at 750°C (as simulated PWHT) has led to the following results:

1. In the as-cast state GP91 cast steel is characterized by a microstructure of auto-tempered martensite with numerous precipitations, such as: M_3C, $M_{23}C_6$ and NbX.
2. Oil quenching from 1040°C leads to the formation of autotempered martensite containing intragranular M_3C and NbX particles.
3. In the microstructure of tempered state and after additional PWHT treatment the $M_{23}C_6$ and MX particles were identified. In the GP91 cast steel after heat treatment two morphology types of MX precipitates were observed: spherical, rich in niobium - NbX and lamellar, rich in vanadium - VX.
4. Performed research allows to propose the following sequence of precipitation process for the examined cast steel:

$$M_3C+M_{23}C_6+NbX \rightarrow M_3C+NbX \rightarrow M_{23}C_6+NbX+VX$$

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