731. Precipitation process in VM12 steel after ageing at 650ºC temperature

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Abstract. The material for research was high chromium martensitic VM12 steel. Test pieces were isothermally aged in the air atmosphere at the temperature of 650ºC and at times up to 5000 hours. Changes in the microstructure were observed and recorded by means of high-resolution electron microscope JOEL JEM 3010 and scanning electron microscopy JOEL 6610LV. Identification of the precipitates was made using extraction carbon replicas and thin foils with the SAED method. Changes in the morphology of precipitates in VM12 steel have been shown in the form of diagrams.

The research aim was to analyze the precipitation processes. The tests were performed on VM12 steel in the as-received condition (after heat treatment) and after 5000 hours of ageing at the temperature of 650ºC.

Keywords: martensitic VM12 steel, precipitation process, carbides.

Introduction

Advancement in the power industry resulted in introducing new generation steels which allow applying higher parameters of operation for the power units, the so-called supercritical parameters – steam temperature of 600÷620ºC and steam pressure of ≥ 25 MPa. Increase in the steam parameters is inherently connected with reducing the emission of pollutants into the atmosphere (mainly CO_2) and raising the thermal efficiency of power units (to ca. 50% as a target) [1].

Applying high steam parameters for power units resulted in introducing new steel grades into the power industry since the previously used steels did not meet such high demands laid for high temperature creep resisting materials. One of the new groups of steels brought into the power industry are high chromium martensitic steels. Martensitic steels were obtained through modification of the chemical composition of steels used so far in the power industry. As a result of carbon content reduction and the introduction of additions and micro-additions, such as: W, V, Nb, N and B into the steel containing 9% Cr and ca. 1% Mo, the steels with high mechanical properties were achieved. Creep resistance in these steels (P/T91, P/T92, E911) is higher by min. ca. 20% than the previously serviced steels. The chromium content on the level of 9% is insufficient since it limits the usage of the abovementioned steels to the temperature of 580 ÷ 600ºC. Higher chromium content on the level of 12% is required in order to provide appropriate resistance to oxidation and gas corrosion during the service at the temperature of 600ºC. On the basis of these assumptions new steel was developed, the X12CrCoWMoVNb12-2-2 (VM12) steel. The VM12 steel was supposed to be characterized by creep resistance higher than in P/T92 steel and oxidation and gas corrosion resistance at the temperature above 600ºC similar to that of austenitic PT 304/ PT 347 steels. However, the performed tests proved that above the 600ºC temperature the steel is characterized by unstable microstructure, which leads to its very fast degradation and as a consequence to a rapid decrease in the creep resistance already after ca. 10 000 ÷ 15 000 hours at the temperature of 650ºC. Therefore, the maximum temperature of operation for those steels has been limited to the temperature of 600 ÷ 620ºC, and the steel is mostly applicable for thin-wall pipes of super-heaters [1 ÷ 5].

The aim of the performed research was to characterize the microstructure and identify the precipitations in new high chromium VM12 (X12CrCoWMoVNb12-2-2) steel in the initial (as-received) condition as well as after ageing for up to 5000 hours at the temperature of 650ºC.

1. Material and methods

The research was carried out on high chromium VM12 (X12CrCoWMoVNb12-2-2) steel with its chemical composition given in Table 1. Test pieces for research were taken out from a section of a pipe with its outer diameter of 355.6mm and wall thickness of 35mm. The VM12 steel under investigation was in the as-received condition (quenched and tempered) and after ageing for up to 5000 hours at the temperature of 650ºC.

Table 1. Chemical composition of VM12 (X12CrCoWMoVNb12-2-2), mass %

Content of elements, mass %												
C	Si	Mn	Cr	Ni	Mo	V	W	Nb	Co	B	N	Ti
0.13	0.48	0.22	11.40	0.19	0.27	0.22	1.30	0.05	1.20	0.003	500 ppm	<0.005

The microstructure of VM12 steel was investigated by means of an optical microscope Axiovert 25 (OM), scanning electron microscope JOEL JSM 6610LV (SEM) and high-resolution transmission electron JOEL JEM – 3010 (TEM). Observation and record of the microstructure was carried out on a conventionally prepared metallographic specimens etched with Villela's reagent.

Identification of precipitates in the examined steel in the as-received condition as well as after 5000 hours of ageing at the temperature of 650ºC was performed by means of extraction carbon replicas and thin foils using the SAED method.

2. Results and discussion

Microstructure of VM12 steel in the as-received condition

VM12 steel in the state after heat treatment (i.e. quench hardening and tempering) was characterized by a typical microstructure of high-temperature tempered martensite with numerous precipitations of carbides precipitated mostly on the boundaries of former austenite grain, as well as on the boundaries and inside the laths of tempered martensite - Fig. 1.

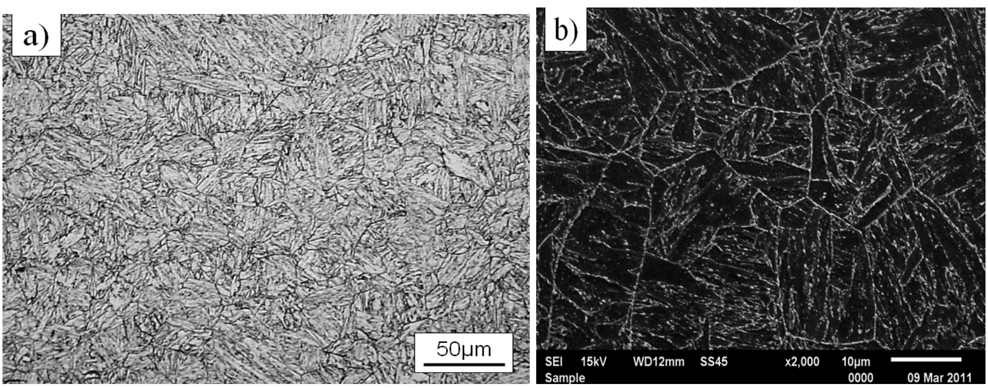

Fig. 1. Microstructure of VM12 cast steel in the as-received condition: a) OM; b) SEM; etched with Villela's reagent

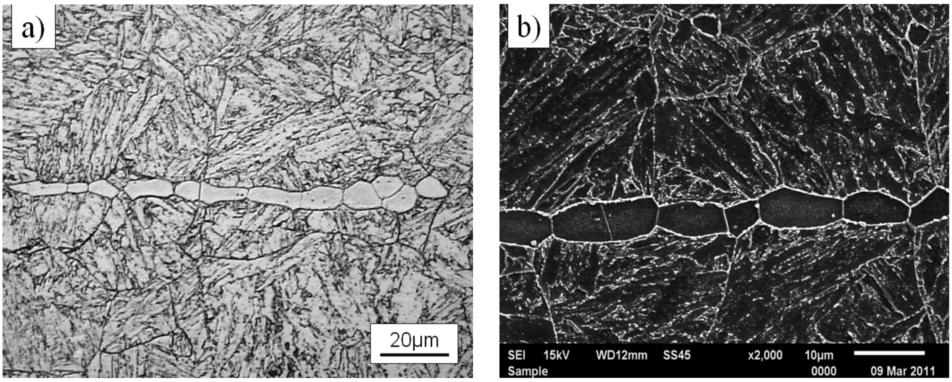

Fig. 2. Microstructure of VM12 steel in the as-received condition with a visible chain of delta ferrite: a) OM; b) SEM; etched with Villela's reagent

In the microstructure of VM12 steel also the presence of δ ferrite is permissible in the amount of no more than 2%. In the case of larger amount of δ ferrite in the microstructure of the examined steel, a considerable deterioration in mechanical properties can be expected, impact strength in particular [5, 6].

Performed identifications of precipitates in the microstructure of investigated VM12 steel in the as-received state revealed two types of precipitates: MX and $M_{23}C_6$. Precipitates of the MX type were mostly precipitated on the dislocations inside the laths and on the lath boundaries of martensite. In the microstructure of the examined steel two morphologies of the MX precipitates were observed: spherical precipitates of NbX type rich in niobium as well as lamellar precipitates of VX type rich in vanadium. Precipitates of NbX during heat treatment inhibit the growth of austenite grain, while together with VX nitrides – precipitated during tempering, they are an effective obstacle for the movement of dislocations, thus providing high creep resistance. Disappearance of this type of precipitates, e.g. as a result of Z phase formation, leads to a very rapid decrease in the creep resistance [2, 4, 5, 7]. Whilst $M_{23}C_6$ carbides (carbonborides) (Fig. 3) stabilizing the subgrain microstructure were disclosed most of all on the boundaries of former austenite grain and on the boundaries of martensite laths. Only some sparse carbides of this type were observed inside martensite laths. Carbides of the $M_{23}C_6$ type were seen also on δ ferrite grain boundary. Hardness of VM12 steel in the as-received condition amounted to 260 HV10.

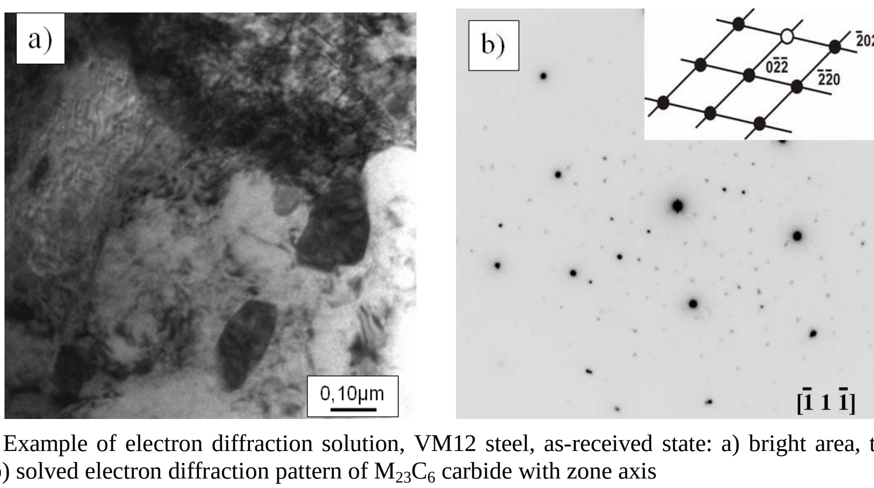

Fig. 3. Example of electron diffraction solution, VM12 steel, as-received state: a) bright area, thin foil, TEM; b) solved electron diffraction pattern of $M_{23}C_6$ carbide with zone axis

The morphology of precipitates of martensitic VM12 steel in the as-received state is presented in a scheme in Fig. 4.

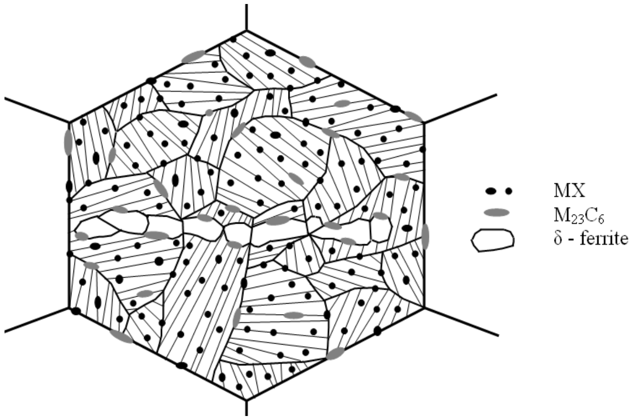

Fig. 4. Scheme of the morphology of precipitates in VM12 steel in the as-received condition (after heat treatment)

Microstructure of VM12 steel after ageing

Fig. 5 illustrates the microstructure of VM12 steel after 5000 hours of ageing at the temperature of 650ºC.

What could be easily noticed was a partial disappearance of lath microstructure of high-temperature tempered martensite. The process of disappearance of the lath structure occurred in the examined steel as a result of recovery and recrystallization of the matrix, causing the growth of grain size. In the microstructure the privileged precipitation of carbides on the boundaries of former austenite grain was revealed. The number of precipitates on former austenite grain boundaries was so large in some areas that they formed the so-called continuous grid of precipitates. On the boundary of δ ferrite grain there were also large precipitates of solid-like shape observed (Fig. 6).

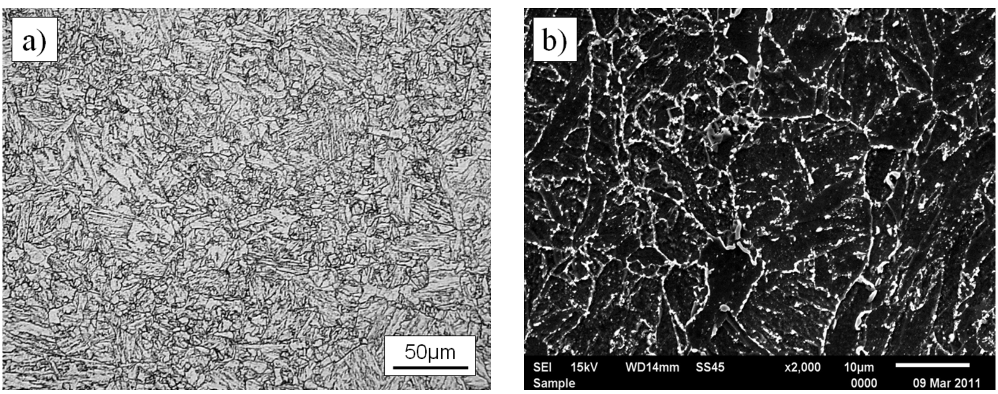

Fig. 5. Microstructure of VM12 steel after 5000 hours of ageing at the temperature of 650ºC: a) OM; b) SEM; etched with Villela's reagent

In the microstructure of investigated steel after ageing one could notice both: areas of polygonized ferrite with numerous carbide precipitates as well as the retained lath microstructure of tempered martensite (Fig. 7).

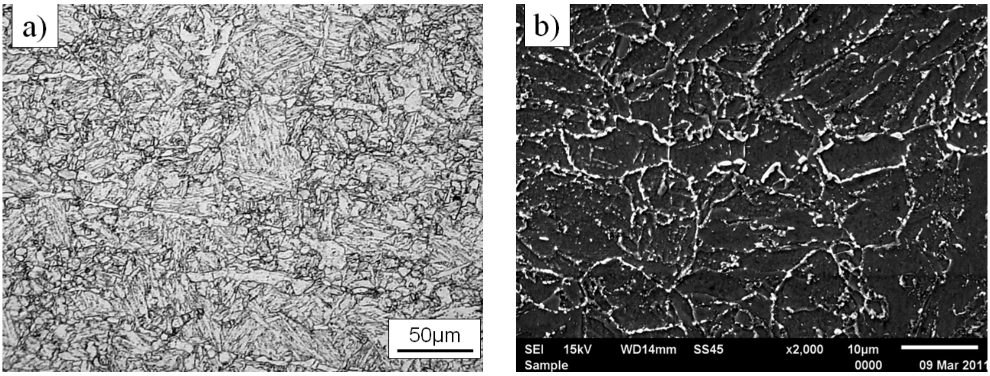

Fig. 6. Microstructure of VM12 steel after 5000 hours of ageing at the temperature of 650ºC: a) OM; b) SEM; etched with Villela's reagent

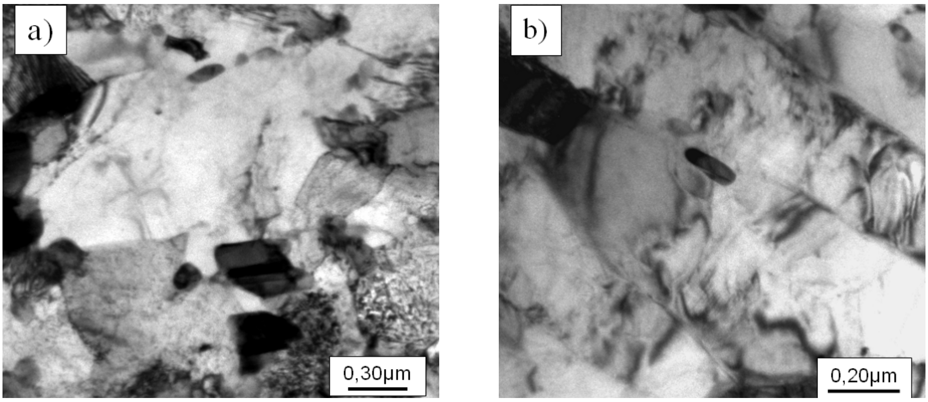

Fig. 7. Microstructure of VM12 steel after 5000 hours of ageing at the temperature of 650ºC, TEM, thin foil

Performed identifications proved that the dominant type of precipitates in the examined steel after ageing (similarly as in the as-received condition) were $M_{23}C_6$ carbides rich in chromium. $M_{23}C_6$ carbides were precipitated, like in the as-received state, mainly on grain boundaries of former austenite grain, on the boundaries of martensite laths and the boundaries of δ ferrite grains. Additionally, inside martensite laths (and also ferrite grains) fine dispersive MX precipitates rich in niobium or/and vanadium were disclosed. At the same time on grain boundaries, usually near $M_{23}C_6$ carbides, the precipitation of Laves phase was noted (Fig. 8). The Laves phase precipitates were seen also on the boundaries of martensite laths. Numerous $M_{23}C_6$ carbides precipitated on grain boundaries (and forming a continuous grid of precipitates in some areas) as well as the Laves phase precipitates may contribute to loss of toughness and increase in the nil ductility transition temperature (reduction in Upper Shelf Energy in the impact tested).

In the microstructure of VM12 steel after ageing, apart from the abovementioned precipitates, there was also single precipitation of Z phase identified – complex Cr (V, Nb) N nitride (Fig. 9). Fine dispersive precipitates of MX in VM12 steel at the temperature of 650ºC are metastable phases, therefore the precipitation of Z phase (more stable in thermodynamic terms) is connected with dissolving of those precipitates in the matrix. Every large precipitation of Z phase occurs as a result of the disappearance of ca. 1500 particles of MX [7, 8]. This process is similar to a change in the stage of ageing of aluminum alloys which leads to a transition from phase ageing (hardening) to over-aging (softening aging). According to [7, 8] initially the niobum – rich carbonitride particles transform to Z phase. Formation and growth of Z phase causes dissolution of Nb(C, N) carbonitrides in the matrix. Secondly, the vanadium – rich carbonitrides transform to Z phase. Precipitation of Z phase as well as Laves phase in the examined steel decreases not only the effectiveness of precipitation strengthening but also solution strengthening, as a result of diffusion of: Cr, Mo, W to the occurring and coarsening (coagulating) particles. This results in the decrease in creep resistance, loss of toughness and growth of nil ductility transition temperature. Whilst the precipitation of Laves phase and Z phase in the microstructure has an insignificant effect on the strength properties, which leads to a decrease in hardness only by ca. 6% in comparison with the as-received condition. Hardness of VM12 steel after 5000 hours of ageing at the temperature of 650ºC amounted to 243 HV10.

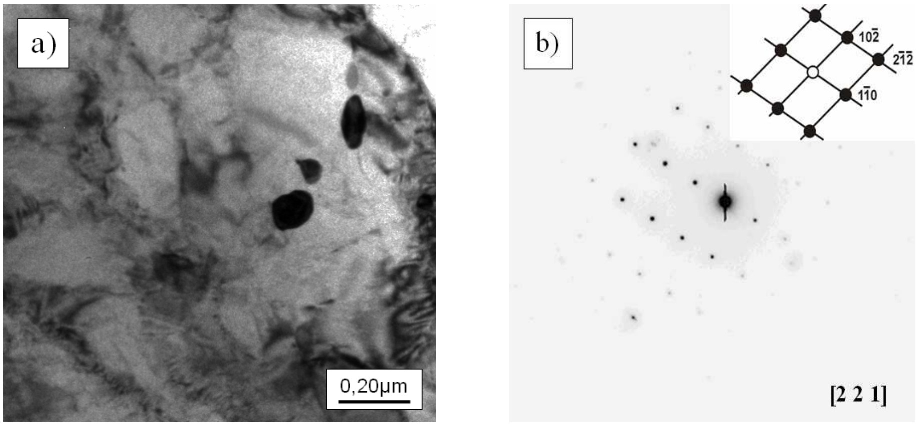

Fig. 8. Example of electron diffraction solution, VM12 steel, 650°C / 5000 h: a) bright area, thin foil, TEM; b) solved electron diffraction pattern of Laves phase Fe_2 (Mo, W) with zone axis

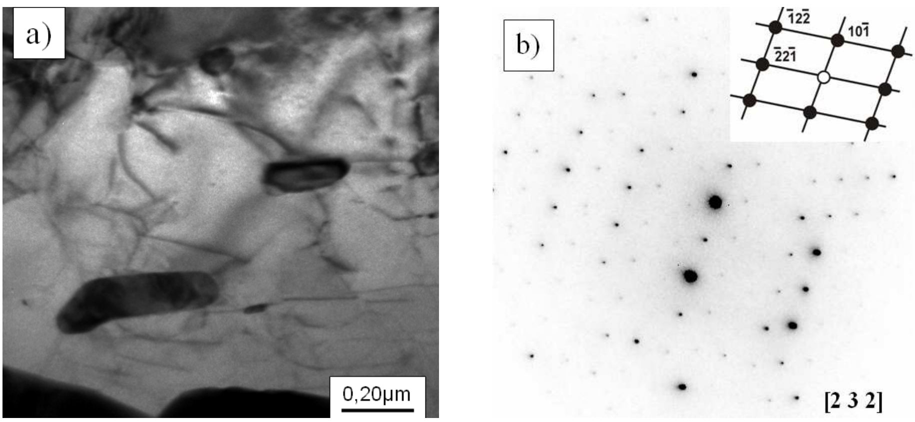

Fig. 9. Example of electron diffraction solution, VM12 steel, 650°C / 5000 h: a) bright area, thin foil, TEM; b) solved electron diffraction pattern of Z phase Cr (V, Nb) N with zone axis

The morphology of precipitates in VM12 steel after ageing is presented in a scheme in Fig. 10.

3. Summary

The subject of research was VM12 steel which belongs to the newly-developed grades of martensitic steels containing ca. 11 ÷ 12% Cr. Performed micro-structural investigations proved that the high chromium VM12 steel in the as-received condition (after quench hardening and tempering) revealed a typical microstructure of tempered martensite with numerous precipitates of the following carbide types: MX and $M_{23}C_6$ and a slight amount of delta ferrite (ok. 2%). Performed identifications of precipitates in VM12 steel in the as-received condition showed that the MX type carbonitrides were precipitated mostly on the dislocations inside the laths and on the lath boundaries of martensite. Whilst $M_{23}C_6$ carbides (carbonborides) were identified first of all on the boundaries of former austenite grain, on the boundaries of martensite laths and on the boundaries of δ ferrite grains. In the as-received state there were two morphologies of MX precipitates observed: spherical precipitates of NbX type rich in niobium as well as lamellar precipitates of VX type rich in vanadium.

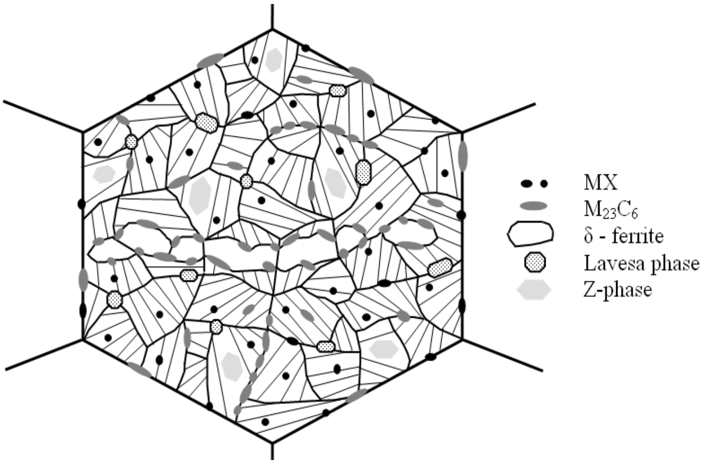

Fig. 10. Scheme of the morphology of precipitates in VM12 steel after 5000 hours of annealing at the temperature of 650ºC

Ageing at the temperature of 650ºC for 5000 hours contributed to the microstructure degeneration in the examined steel through: partial disappearance of lath microstructure of tempered martensite, growth of the sub-grain size and fall of the dislocation density as a result of the processes of matrix recovery – in the microstructure of VM12 steel after ageing one could notice: the retained lath microstructure of tempered martensite with high density of dislocations and the polygonized ferrite grains, these structures alternated with each other, as well as the privileged precipitation of $M_{23}C_6$ carbides not only on grain boundaries of former austenite grain but also on the boundaries of δ ferrite grains. In some areas the amount of precipitated carbides was so big that they formed the so-called continuous grid of precipitates. The continuous grid of precipitates on grain boundaries and the size growth of $M_{23}C_6$ carbides precipitated on those boundaries have a very unfavorable influence on the examined steel's ductility. Moreover, in the microstructure of VM12 steel after ageing the precipitation of Laves phase and Z phase was disclosed. Laves phase was noticed mainly on grain boundaries, often near $M_{23}C_6$ carbides. Z phase – complex nitride, Cr (V, Nb) N, (more stable in thermodynamic terms) in the investigated steel occurred at the expense of disappearance of very favorable fine-dispersive precipitates of the MX type. After 5000 hours of ageing also single Z phase precipitates were disclosed. The precipitates of Z phase and Laves phase and the coagulation of $M_{23}C_6$ carbides contribute to the decrease in effectiveness of precipitation strengthening and solution strengthening, thereby causing a reduction in creep resistance and fall of ductility in VM12 steel.

Performed research allows proposing the following precipitation sequence for VM12 steel aged for 5000 hours at the temperature of 650ºC:

As-received conditions		5000 h/650°C
$M_{23}C_6$ + MX	→	$M_{23}C_6$ + MX + Laves Phase + Z Phase

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