Archives
of Materials Science
and Engineering

Volume 113
Issue 1
January 2022
Pages 5-12

International Scientific Journal
published monthly by the
World Academy of Materials
and Manufacturing Engineering

DOI: 10.5604/01.3001.0015.6966

Modern heat-resistant 11%Cr martensitic steel for power industry

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ABSTRACT

Purpose: The purpose of the investigations was to characterise and describe the modern creep-resistant Thor 115 steel for supercritical power units.

Design/methodology/approach: The investigations were performed based on the knowledge and experience of the author, the preliminary results of his own research and the available literature on the subject-matter of the considerations presented in the paper.

Findings: Modern steel Thor 115 was subjected to overall analysis in terms of its use as a potential heat-resistant structural material for power plant components. Based on the preliminary results of own research and the available literature data, it has been shown that the analysed steel may be a structural material of full value if the assumed creep resistance in the service temperature range of 600-650°C is confirmed.

Research limitations/implications: The comprehensive analysis of degradation of microstructure of the steel after ageing (and/or creep) requires TEM examinations. Finding the correlation between the creep and ageing conditions and changes in the microstructure of the steel.

Practical implications: The investigations carried out as part of the paper and the considerations on the subject-matter of the analysed steel may be the basis for the development of a database of material characteristics for steels, alloys and welded joints.

Originality/value: The analysis of chemical composition, heat treatment and mechanical properties and the investigations of microstructure of Thor 115 steel are presented.

Keywords: Thor 115 steel, Chemical composition, Microstructure, Mechanical properties

Reference to this paper should be given in the following way:

G. Golański, Modern heat-resistant 11%Cr martensitic steel for power industry, Archives of Materials Science and Engineering 113/1 (2022) 5-12.

DOI: https://doi.org/10.5604/01.3001.0015.6966

MATERIALS

1. Introduction

The development of conventional power generation requires increasing the efficiency of power units, is related to increasingly stringent environmental requirements, and depends primarily on the availability of the construction materials with adequate properties. These materials must show high creep resistance with sufficient corrosion

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resistance in both the steam and exhaust gas atmosphere. At the same time, they must be capable of being processed to allow the boiler pressure part components and the main steam pipelines to be made out of them [1,2].

In modern and modernised power units, high-chromium martensitic steels are among the basic heat-resistant construction materials. Such steels have been used for the individual stages of steam superheating in boilers – both their chambers and coils, where the predominant destruction process is the creep. These materials are also used for the main primary and secondary steam pipelines [2-5].

Two types of these alloys are distinguished in the group of martensitic steels: 9Cr steels and 12Cr steels. The typical representatives of these groups of materials are P91 and P92 steels and VM12 steel, respectively. The development of these alloys has been mainly related to the modification and optimisation of their chemical compositions, but also to the parameters of heat (heat and plastic) treatment. The maximum service temperature of these steels is 620°C, which is due to insufficient high-temperature corrosion resistance for 9Cr steels and microstructure instability for 12Cr steels [5-7].

The use of machines and equipment made of martensitic steels under creep conditions results in changes in the microstructure, the effect of which is a reduction in their performance. The main microstructure degradation mechanisms for high-chromium martensitic steels are: the coagulation of $M_{23}C_6$ carbides and the precipitation and growth of the Laves-phase and Z-phase particles. The $M_{23}C_6$ particles are precipitated during tempering and their main role is to stabilise the lath microstructure of tempered martensite. The increase in the size of these particles during service leads to a reduction of this effect and consequently to the accelerated recovery and recrystallisation of the matrix [6,8]. The Laves phase is precipitated during service leading not only to matrix depletion of substitution elements, but its occurrence in the matrix also results in a significant increase in brittleness [5,7,9]. The precipitates of this phase have a negative effect on the creep resistance of martensitic steels as well [10]. Similarly to the Laves phase, the Z phase is also precipitated during service due to the MX → Z phase transformation. In martensitic steels, the dispersion MX precipitates are responsible for inhibition and reduction of dislocation mobility, which affects the creep resistance. However, the MX precipitates in 12Cr steels are metastable and disappear at the cost of Z-phase particles at above 600°C. It is assumed that a single Z-phase precipitate consume approx. 1500 MX particles. The disappearance of MX precipitates in favour of Z-phase particles leads to a significant drop in creep resistance, which is reflected in a reduction of safe service time. The rate of MX → Z-phase transformation depends not only on the temperature, but also on the content of chromium as well as niobium in martensitic steels [11-13]. High content of these elements in the martensitic steel leads to a reduction in the time of transformation of precipitates. As demonstrated in [14], single Z-phase precipitates do not reduce the creep resistance of 9Cr steels.

The microstructure instability of 12Cr steel was one of the reasons for the implementation of heat-resistant austenitic steels in the power industry. In spite of a number of advantages, including but not limited to good/very good corrosion resistance and high creep resistance, the austenitic steels have unfavourable physical properties and are susceptible to intergranular and stress corrosion [15,16]. The high price of these materials also plays an important role. Therefore, many development and research centres are working to improve the stability of martensitic steels to enable them to be used in power units operating at above 600-620°C [5,7]. One of the grades of these modern heat-resistant materials that are designed to meet these expectations is 11%Cr steel designated as Thor 115 (T115) the characteristics of which are the subject of this article.

2. Chemical composition

The required chemical composition of the T115 steel is summarised in Table 1. As compared to the P91, the modification of the chemical composition of the test steel consisted of the increase in the chromium content and the reduction in the amount of molybdenum and niobium, as well as the introduction of the micro-addition of boron [17,18]. Increasing the chromium content to approx. 11% in this steel is intended to provide the adequate heat resistance at the anticipated service temperature (Fig. 1). At the same time, this concentration of chromium limits the rate of the Z-phase precipitation, which corresponds to that of the MX → Z phase transformation in the P91 steel (Fig. 2) [19].

Table 1.
Comparison of the required chemical composition of T115 and P91, wt.% [20,21]

Steel	C	Mn	Si	Cr	Mo	Ni	V	Nb	N	B
T115	0.08-0.13	0.20-0.50	0.15-0.45	10.00-11.00	0.40-0.60	max 0.25	0.18-0.25	0.02-0.06	0.030-0.070	max 0.005
P91	0.08-0.12	0.30-0.60	0.20-0.50	8.00-9.50	0.85-1.05	max 0.40	0.18-0.25	0.06-0.10	0.030-0.070	---

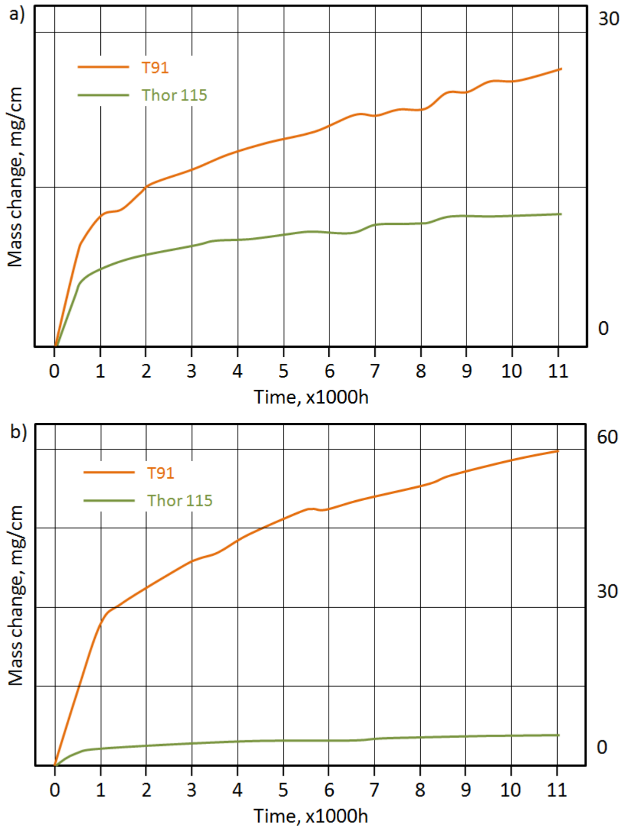

Fig. 1. Mass change due to steam oxidation of T115 and P91 steel at: a) 600°C; b) 650°C [22]

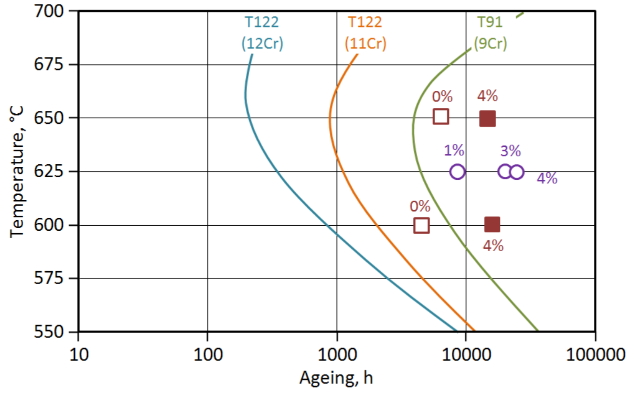

Fig. 2. Comparative diagram of time-temperature-precipitation for Z phase of Thor 115 steel and commercial grades [19]

The purpose of the reduction in niobium content of the test steel was also to slow down the precipitation of this harmful phase. The research [13] shows that the absence of niobium-rich precipitates significantly inhibits the precipitation of the Z phase. In turn, the reduction in molybdenum concentration (compared to P91 steel) was expected to affect the delay of the nucleation process and the growth of the Laves-phase precipitates. However, the lower content of this high-melting element (melting point of molybdenum is 2623°C) may have a negative impact on the stability of the dislocation martensitic matrix and consequently speed up the recovery and polygonisation processes during service. The micro-addition of boron introduced into the martensitic steel results in the precipitation of $M_{23}(C, B)_6$ carboborides with higher thermodynamic stability compared to that of $M_{23}C_6$ carbides (Tab. 2). This ensures a slower coagulation of these precipitates, which improves the stabilisation of the tempered lath martensite microstructure during service. At the same time, this element also has a positive effect on the increase in stability of the Laves phase by limiting the rate of its coagulation [5,17,18].

Table 2.
The effect of boron content on the coagulation coefficient K_d of $M_{23}C_6$ carbides and Laves-phase precipitates in 9Cr-2.7W-3Co-V-Nb-N-xB steel aged for 1000-5000h at 650°C [17]

Boron content, wt%	x		
	0	0.006	0.014
$M_{23}C_6$ carbides	$9.2 \cdot 10^{-29}$	$6.5 \cdot 10^{-29}$	$4.5 \cdot 10^{-29}$
Laves phase	$2.6 \cdot 10^{-28}$	$2.4 \cdot 10^{-28}$	$2.3 \cdot 10^{-28}$

3. Heat treatment of T115 steel

The recommended heat treatment parameters for T115 steel are presented in Table 3. Heat treatment of the steel consists of the air-quenching (also called normalising) and the high tempering. High austenitising temperature of the test steel, but also of P91, higher than 1000°C, is essential to dissolve $M_{23}C_6$ carbides (carboborides) and part of the MX precipitates (rich mainly in vanadium) in the matrix. However, the MX precipitates rich mainly in niobium, are not partially dissolved, thus preventing the growth of austenite grain. The grain refinement has a positive effect on the strength properties and toughness of this group of steels [5,7,23].

The dissolution of most precipitates in the matrix during the austenitising process results in its saturation with carbon and alloying elements. It causes a very high durability of supercooled austenite, thus providing this group of steel with high hardening capacity. The selection of the optimum austenitising temperature of martensitic steels not only affects their basic mechanical properties, but – in case of T115 steel – also has an impact on the reduction in NbC precipitates after toughening (Fig. 3) [19].

Table 3.
Recommended heat treatment parameters for T115 and P91 steel [20,21]

Steel grade	Heat treatment parameters	
	Quenching from austenitising temperature, °C	Tempering, °C
Thor 115	1060-1100	750-790
P91	1040-1090	730-780

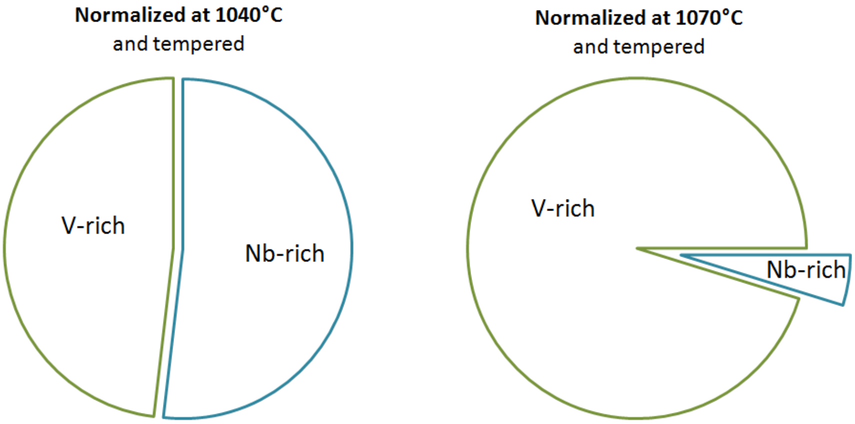

Fig. 3. Effect of austenitising temperature on volume fraction of MX precipitates in microstructure of T115 steel after tempering [19]

Table 4.
Required mechanical properties of Thor 115 and P91 steels at room temperature [20,21]

Steel grade	YS MPa	TS MPa	El., %		KV, J	
			longitudinal	transverse	longitudinal	transverse
Thor 115	450	620-850	19	17	68	41
P91	450	630-830	19	17	40	27

Unlike VN particles, the niobium-rich MX precipitates are transformed into the Z phase faster [13]. This is due to the lower thermodynamic stability of NbC precipitates compared to that of the VN particles whose value expressed as the enthalpy of formation amounts to -70 and -125 kJ/mol, respectively [24]. Decreasing the fraction of these precipitates in the microstructure reduces a future negative impact of the Z-phase particles on the properties of this steel.

The tempering of quenched steel is intended to impart a relatively high initial microstructure stability to this steel and obtain the required mechanical properties. A lower tempering temperature provides higher strength properties with lower plastic properties and ductility, while a higher temperature allows better yield and impact strength to be obtained at the expense of a reduction in strength properties. The higher tempering temperature range of T115 compared to that of P91 provides at least initial higher microstructure stability with properties comparable to those of P91 (Tab. 4).

4. Functional properties of T115 steel

The required basic mechanical properties of the analysed steel are comparable to those of other 9-12Cr martensitic steel grades (Tab. 4). Also, the value of the yield strength at elevated temperature and creep resistance are similar to the properties of P91 steel (Fig. 4).

The mechanical properties of steel depend on the contribution and impact of individual strengthening mechanisms affecting the resulting values of specific parameters. The role of individual strengthening mechanisms is usually related to the yield strength increase for a given steel grade. According to [25], the predominant mechanisms determining the properties (yield strength) in 9-12%Cr martensitic steels in the as-received condition are the grain boundary, lath boundary, sub-boundary and solid solution strengthening by substitution atoms (Cr, Mo, W). And according to [26], the properties of steels in this group are initially affected mostly by the grain boundary, lath boundary, sub-boundary and dislocation strengthening. The mechanical properties of T115 martensitic steel which are similar to those of other grades in this group of materials (Tab. 4, Fig. 4) indicate the resulting properties that are similar in terms of the form and share of individual strengthening mechanisms.

Whereas the higher chromium content of this steel compared to that of 9Cr steel (Tab. 1) results in better heat resistance, both at 600 and 650°C – Figure 1.

5. Microstructure of T115 steel in the as-received condition

In the as-received condition, the T115 martensitic steel has a microstructure of tempered martensite with a retained lath structure, relatively high density of dislocation within subgrains and numerous precipitates (Fig. 5). In the test steel in the as-received condition, the $M_{23}C_6$ and MX precipitates are mainly observed (Fig. 6). The $M_{23}C_6$ carbides are precipitated mainly at the prior austenite grain boundaries and at the lath/subgrain boundaries (Fig. 5). Few of them are visible within martensite laths. The $M_{23}C_6$ carbides in steels of the 9-12%Cr type are the dominant precipitation and constitute around 90% of all particles in these steels [5,6]. The purpose of these particles is to stabilise the tempered lath martensite microstructure which, according to [2, 5-7, 14], has a major impact on the slowing down of the matrix polygonisation processes. The predominant MX precipitates in T115 steel are VN particles (Fig. 7), but in microstructure of the steel NbC-rich carbides are observed as well.

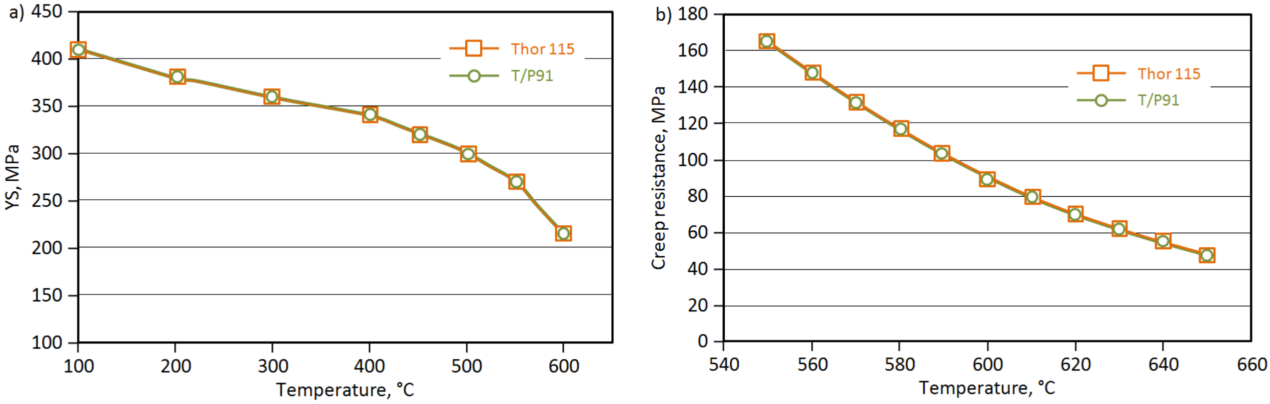

Fig. 4. Effect of test temperature on change in: a) yield point; b) creep strength of Thor 115 and P91 steels [20,21]

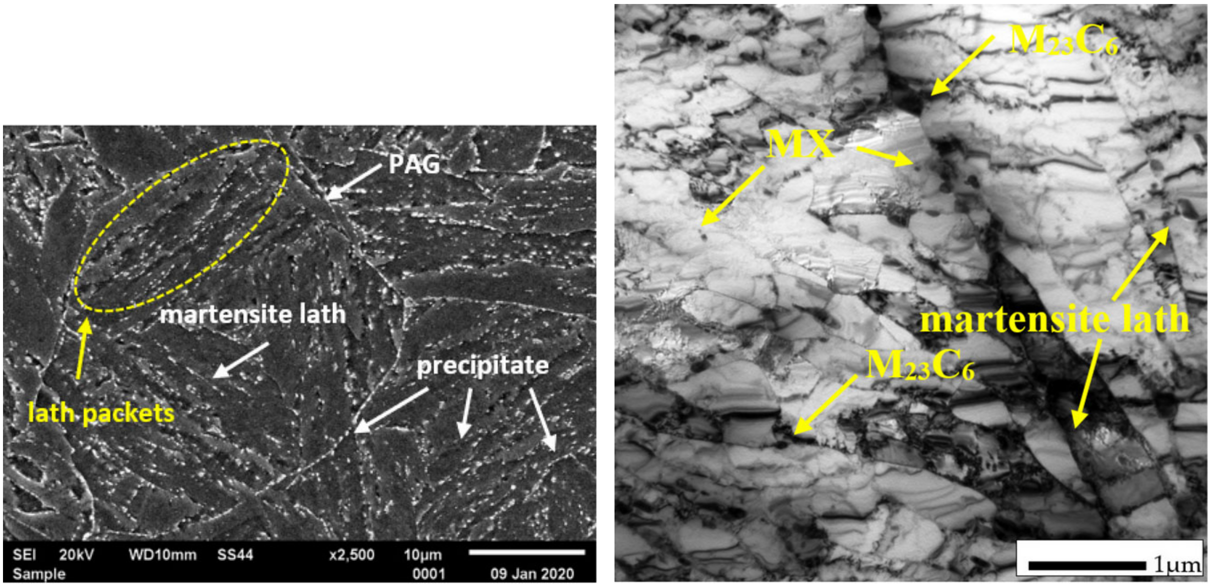

Fig. 5. Microstructure of Thor 115 steel in the as-received condition: a) SEM; b) TEM [28]

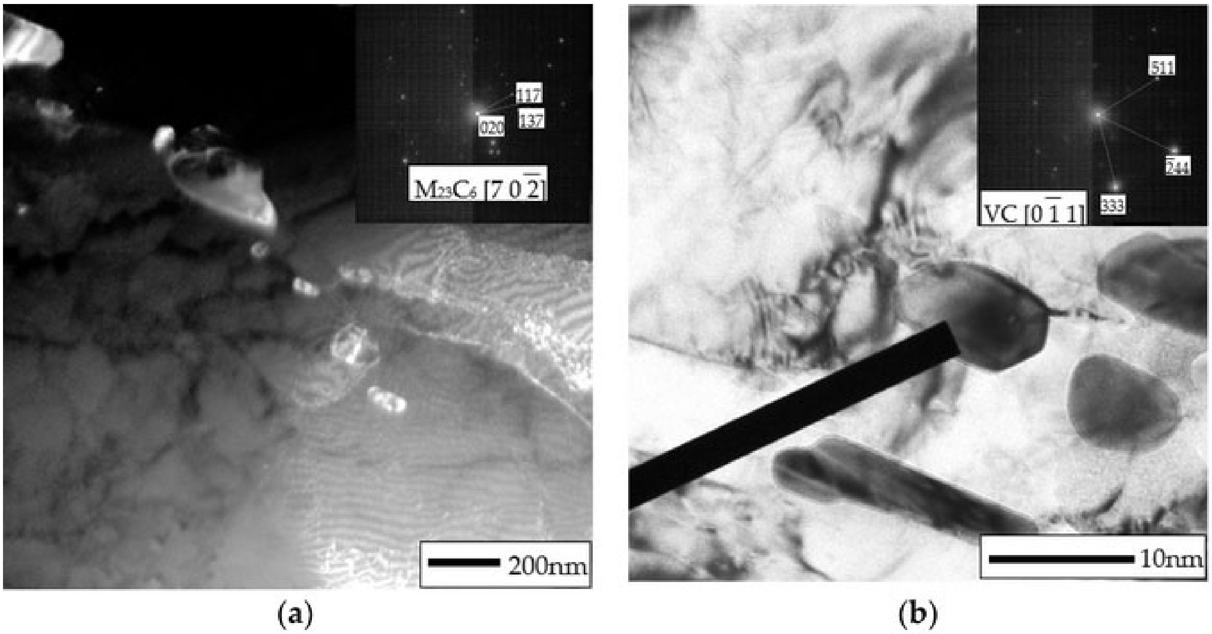

Fig. 6. Precipitates in Thor 115 steel in the as-received condition: (a) $M_{23}C_6$; (b) MC [28]

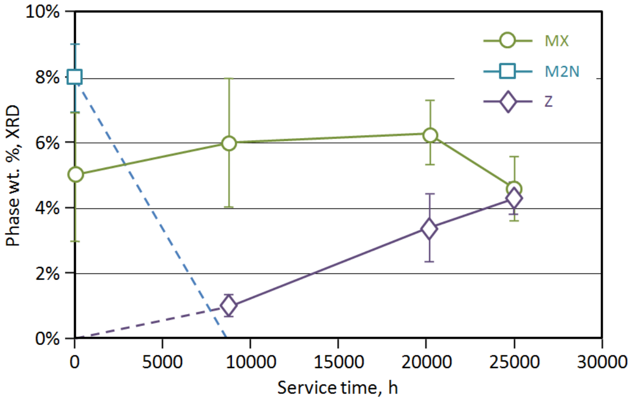

Fig. 7. Effect of service time of T115 steel at 625°C on the percentage change in the fraction of precipitates [27]

The dispersion VN particles are precipitated on dislocations within subgrains and at the subgrain boundaries. Their purpose is to restrict the free movement of dislocation. In turn, the role of NbC precipitates is mainly limited to the inhibition of grain growth during the heat treatment [5-7, 14]. Thermal stability of the MX precipitates in steels of the 9%Cr type is very high. The coagulation rate of the MX precipitates in the temperature range of 500-600°C amounts to around one-tenth of the coagulation rate of the $M_{23}C_6$ carbide. Whereas in martensitic steels of the 12%Cr type, the MX particles are metastable precipitates that undergo a transition into Z phase during the service [6,12,24].

According to [27], also M_2N precipitates can be observed inside the laths/subgrains in the microstructure of T115 steel. In martensitic steels, they are treated as metastable precipitates which undergo an "in situ" transformation into Z-phase particles during service (Fig. 7).

6. Conclusions

Modern steel Thor 115 was analysed for chemical composition, heat treatment parameters, mechanical properties and microstructure. The chemical composition of the test steel was designed to provide the adequate heat resistance at the service temperature above 600-620°C, while limiting the harmful effects of the Laves and Z phases. The literature data [27] and the preliminary results of own research, i.e. ageing for up to 20,000 h [29], indicate that the course and degree of changes in mechanical properties of Thor 115 steel in the temperature range of 600-650°C are similar to those of other grades of martensitic steels. This indicates a similar microstructure stability of these steels, which can make Thor 115 a structural material of full value in the event that the assumed creep resistance is confirmed. However, a decrease in the volume fraction of the MX particles and growth of Z phase precipitates shown in Figure 7 may raise some concerns. As experience shows [5-7, 12], a significant drop in the volume fraction of the dispersive MX particles in the microstructure of serviced martensitic steels leads in consequence to the fall of their creep resistance.

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