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THE EFFECT OF AGEING TEMPERATURES ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF GX12CrMoVNbN9-1 (GP91) CAST STEEL

WPŁYW TEMPERATURY STARZENIA NA MIKROSTRUKTURĘ I WŁAŚCIWOŚCI MECHANICZNE STALIWA GX12CrMoVNbN9-1 (GP91)

Increase in the steam parameters, the so-called supercritical parameters, resulted not only in the growth of efficiency of power units, or reduction in the emission of pollutants into the atmosphere, but also it has contributed to the development of heat-resisting steels and cast steels. One of the newly developed and implemented cast steels in the power industry is martensitic GX12CrMoVNbN9-1 (GP91) cast steel, created on the basis of chemical composition of P91 steel. The cast steel of a microstructure and properties similar to the base material replaces in the power industry the grades of steel used previously which do not meet the increasingly high requirements. A study has been made with regard to the effects of ageing at 550 and 600°C and time up to 6000 hrs on the changes in microstructure and mechanical properties of GX12CrMoVNbN9-1 (GP91) cast steel. A detailed microstructural research and the analysis of secondary phases was carried out using the electron microscopy technique, whilst the research on mechanical properties included a hardness test, static tensile test and impact strength measurement. The microstructural observations showed that the lath martensite microstructure was maintained after 6000 hrs. The coarsening of $M_{23}C_6$ carbides was revealed. Ageing of the investigated cast steel resulted in a slight decrease in the strength properties ($Rp_{0.2}$, TS and HV30), i.e. of around 6%, which was accompanied by a significant decrease in impact strength KV. Moreover, in the microstructure of investigated cast steel there were the processes of recovery and polygonization of the matrix observed.

Keywords: GX12CrMoVNbN9-1 cast steel, ageing process, microstructure, mechanical properties

Wzrost parametrów pary do tzw. parametrów nadkrytycznych skutkował nie tylko wzrostem sprawności bloków energetycznych, czy też zmniejszeniem emisji zanieczyszczeń do atmosfery, ale również przyczynił się do rozwoju stali i staliw żarowytrzymałych. Jednym z nowoopracowanych i wdrożonych do energetyki staliw było martenzytyczne staliwo GX12CrMoVNbN9-1 (GP91), które powstało na bazie składu chemicznego stali P91. Staliwo to o mikrostrukturze i właściwościach zbliżonych do materiału bazowego zastępuje w energetyce dotychczas stosowane gatunki staliw, które nie spełniają coraz to wyższych wymagań. W pracy przedstawiono badania wpływu starzenia w temperaturze 550 i 600°C oraz czasach wytrzymania do 6000 godzin na zmiany w mikrostrukturze i właściwościach mechanicznych staliwa GX12CrMoVNbN9-1 (GP91). Badania mikrostruktury staliwa GP91 w stanie wyjściowym oraz po starzeniu przeprowadzono za pomocą mikroskopii świetlnej i elektronowej. Wpływ temperatury i czasu starzenia na właściwości badanego staliwa określono za pomocą pomiaru twardości, statycznej próby rozciągania oraz próby udarności. Przeprowadzone badania wykazały: proces zdrowienia i poligonizacji osnowy oraz koagulację wydzieleń $M_{23}C_6$. Zmiany w mikrostrukturze zachodzące w czasie starzenia w niewielkim stopniu wpłynęły na właściwości wytrzymałościowe (HV30, $R_{p0,2}$, R_m), natomiast przyczyniły się do znacznego spadku udarności KV badanego staliwa.

1. Introduction

Development of the power industry, connected with increasingly high demand of mankind for electric energy, and the legal condition related to the limitations on the emission of pollutants into the atmosphere, were an impulse for increasing the efficiency of power units. Growth of the efficiency is connected with the rise in the steam parameters – temperature and pressure to the so-called super- or ultra supercritical parameters. Increase in the parameters of steam was possible due to the development of high temperature creep resisting materials for the power industry. As a result of modification in the chemical composition of previously used steels in the power industry there were two new groups of high temperature creep resisting steels developed, the so-called martensitic steels and bainitic steels [1÷4]. Apart from the above-

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mentioned steel groups for the power industry, also new grades of cast steel were introduced. These cast steels are to replace the so far used low-alloy steel casts Cr-Mo or Cr-Mo-V which do not fulfill high demands laid for the casts designed for service at the increasingly high parameters. One of these materials is high-chromium martensitic GX12CrMoVNbN9-1 (GP91) cast steel. The GP91 cast steel was created on the basis of chemical composition of X10CrMoVNb9-1 (P/T91) steel, well tested, with stable properties determined and characterized by similar microstructure and mechanical properties as the base material [5÷7].

Long-term service of steels/cast steels at elevated temperature results in a degradation of the microstructure – processes of softening of tempered martensite and decline in mechanical properties. Hence the dependence between changes in the microstructure and their influence on properties is particularly important for these materials [8, 9]. The paper presents the analysis of changes in the microstructure and mechanical properties of GX12CrMoVNbN9-1 cast steel subject to ageing at the temperature of 550 and 600°C at times up to 6000 hours.

2. Material for investigation

Material for investigation was high-chromium martensitic GX12CrMoVNbN9-1 (GP91) cast steel. Chemical composition of the examined cast steel is given in Table 1.

TABLE 1
Chemical composition of GP91 cast steel, %mass

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

The GP91 cast steel for investigation was heat treated: 1040°C/12 h/oil + 760°C/12 h/air + 750°C/8 h/furnace, denominated in this paper as the as – received condition. The last step at 750°C in heat treatment was given to simulate a Post Weld Heat Treatment (PWHT). The samples were isothermally long – term aged in the air atmosphere at the temperature of 550 and 600°C in a laboratory at times to 6 000 hrs.

3. Experimental procedure

Microstructure was characterized by Axiovert 25 optical microscopy (OM) and JOEL JEM – 3010 transmission electron microscopy (TEM) using thin foils and carbon extraction replica. Tensile properties were carried out on the as – received and aged materials at 550 and 600°C up to 2000 and 6000 hrs using cylindrical specimens of 8 mm diameter with gauge length of 40 mm. The specimens were tested at room temperature. Vickers hardness measurement at 30kG (294.3 N) load were carried out at room temperature on the as – received and aged materials. The Charpy impact tests were conducted on the as – received and aged materials using V – noted standard specimens.

4. Results and discussion

4.1. Microstructure and mechanical properties of the GP91 cast steel in the as – received condition

An example of microstructure of GP91 cast steel in the as-received condition is presented in Fig. 1. The microstructure of the GP91 cast steel after heat treatment consists of the tempered martensite laths of large dislocation density and polygonal ferrite grains – these two types of microstructure alternated with each other (Fig. 1b). Between the laths as well as the subgrains the dislocation boundaries occurred. The average size of prior austenite grain was about 25 μm (8 ASTM), whilst the mean diameter of subgrain amounted to 0.708±0.258 μm, at the dislocation density amounting to 2.95±2.02 $\cdot 10^{14}\,m^{-2}$. The detailed microstructure characterization by SEM and TEM of the GP91 cast steel in the as – received condition is described in Ref. [10].

The tempering and annealing treatment produced large amounts of carbide precipitation distributed preferentially along grain and lath boundaries, however, precipitates appeared also in the bulk of the martensite laths microstructure. The main precipitation consists of $M_{23}C_6$ precipitates of the mean diameter amounting to 127nm, located preferentially along/on grain and lath subgrain boundaries (Fig. 2). Few carbides of this type were seen also inside ferrite subgrains.

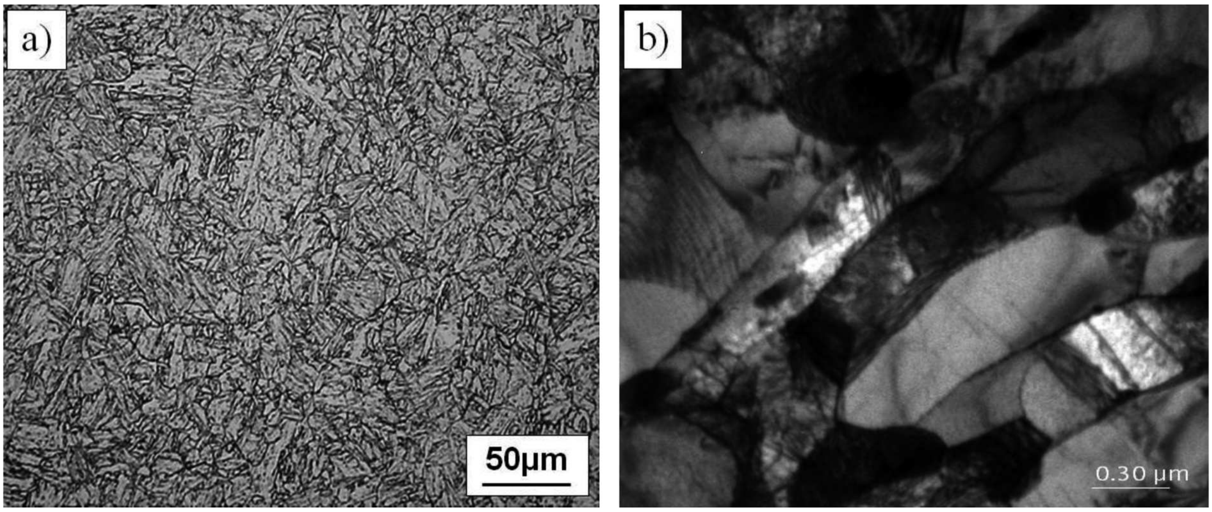

Fig. 1. Microstructure of GP91 cast steel in the as-received condition: a) OM, b) TEM

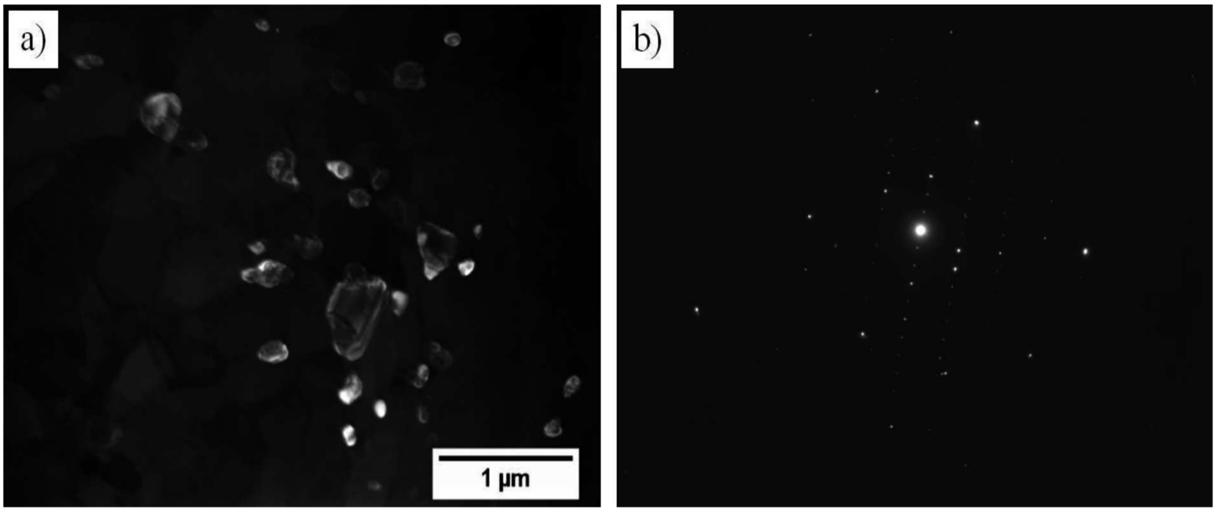

Fig. 2. Morphology of M_{23} C_6 carbides in GP91 cast steel in the as-received condition, a) dark area from the reflection $(4\bar{2}0)_{M23C6}$; c) electron diffraction pattern SAED, $[\bar{1}23]_{M23C6}$ and $[\bar{3}\bar{3}1]_{\alpha}$

Larger carbides of $M_{23}C_6$ were observed on the boundaries of former austenite grain compared to the carbides nucleating on the boundaries. The differences probably result from low energy of wide-angle boundaries of grains of prior austenite and their large stability. Similar observations are presented inter alia in the works [11, 12]. Their morphology varied from globular and cylindrical shape to irregular geometrical shapes. Volume fraction of $M_{23}C_6$ carbides in high-chromium steels/cast steels is estimated on the level of ca. 0.2%, and the $M_{23}C_6$ carbides play a significant role in these alloys – they stabilize the subgrain microstructure of martensite and inhibit the movement of dislocation boundaries e.g. during creep process.

In the as – received state other types of precipitates (MC, MX type) rich in Nb or V, with the size of around 18 nm, have been indentified. They are mainly located inside the subgrains (on dislocation) but also they were seen on the boundaries of laths and subgrains. Two types of MX morphologies have been distinguished in the cast steel after heat treatment: carbonitrides rich in niobium, of the shape close to spherical – NbX as well as plate-like carbonitrides, nitrides rich in vanadium of VX type. It is well known that MX type precipitates are considered to be very useful for long term creep resistance at elevated temperatures. Disappearance of this type of precipitates in the microstructure of high-chromium steels/cast steels, e.g. as a result of precipitation of a complex nitride Cr(V, Nb)N – the Z phase, leads to a very quick, sudden decrease in the creep strength of these materials [13]. The detailed precipitate characterization in the GP91 cast steel after different heat treatment is described in Ref. [14].

Table 2 presents mechanical properties of GP91 cast steel in the as-received condition along with their minimum requirements. Mechanical properties of the investigated cast steel in the as-received condition were higher than the minimum required. Values of the yield strength and tensile strength were higher by ca. 5% with the impact strength over 4 – fold higher than the minimum values required.

High impact strength KV >100 J of the examined cast steel in the as-received condition is demanded because, as proven by the individual study [8], as well as by the literature data [9, 15], during operation at elevated temperatures the decrease in impact strength occurs quicker as compared with the strength properties.

TABLE 2
Mechanical properties of GP91 cast steel after heat treatment

	TS MPa	**YS MPa**	**El. %**	**KV J**	**HV30**
GP91	632	468	26	124	209
Requirement according to [18]	600 ÷ 750	min 450	min 15	min 30	—

4.2. Microstructure and mechanical properties of the GP91 cast steel after thermal ageing

Typical microstructure of the GP91 cast steel after ageing at 550 and 600°C for 6000 hrs are shown in Fig. 3 and 4.

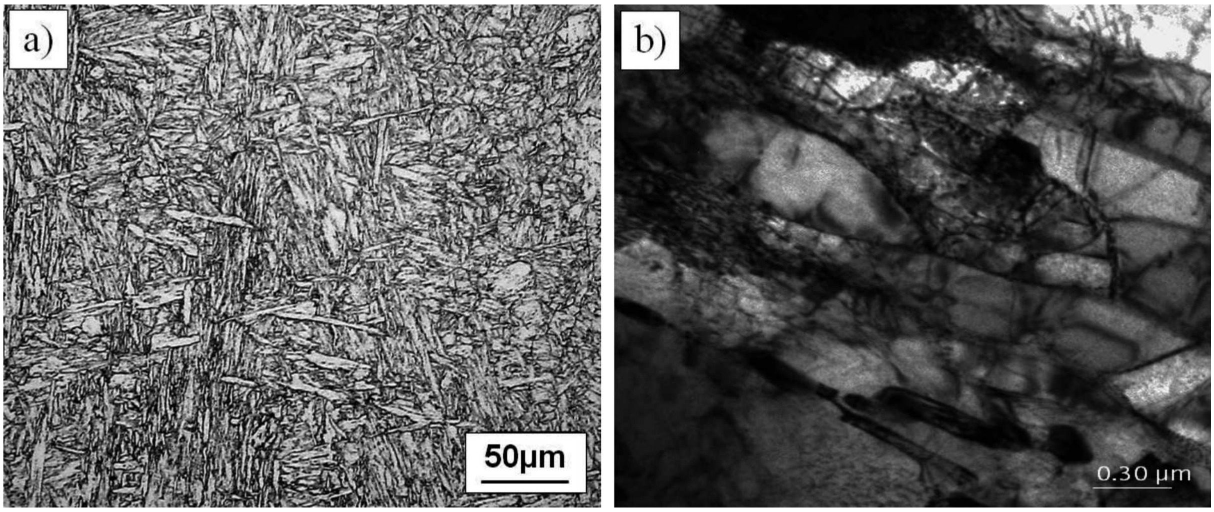

Fig. 3. Microstructure of GP91 cast steel after 6 000 hours of ageing at the temperature of 550°C: a) OM, b) TEM

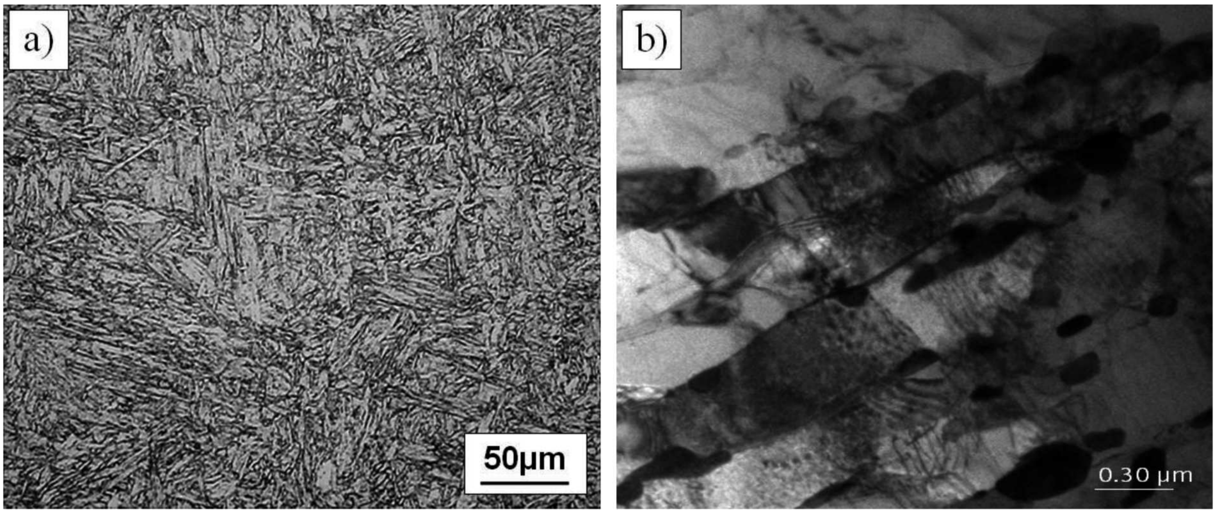

Fig. 4. Microstructure of GP91 cast steel after 6 000 hours of ageing at the temperature of 600°C: a) OM, b) TEM

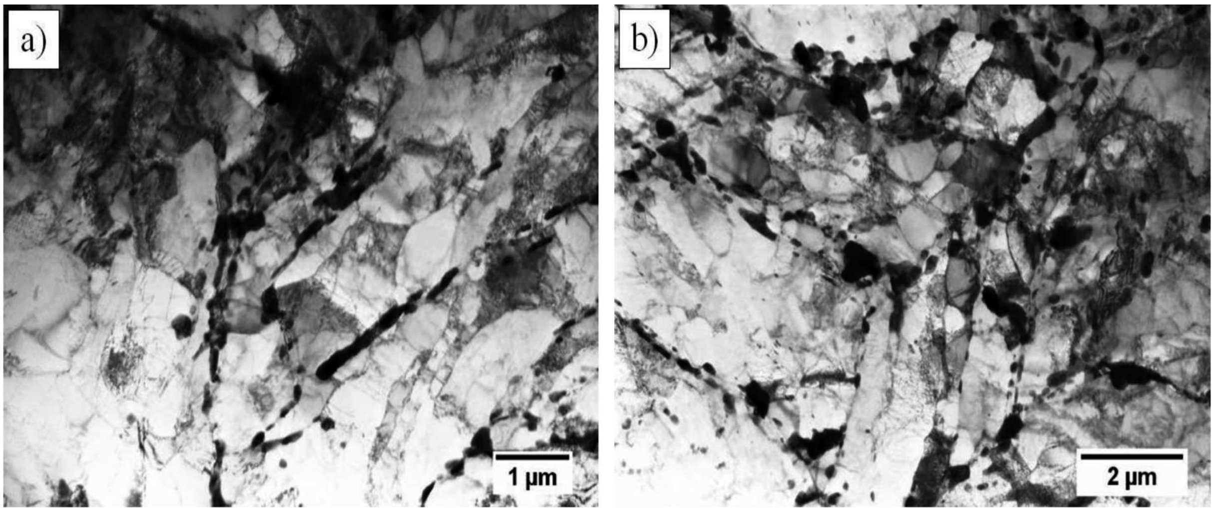

Fig. 5. Precipitations of $M_{23}C_6$ carbides in GP91 cast steel after ageing at the temperature of: a) 550°C; b) 600°C

After ageing the GP91 cast steel was still characterized by a microstructure of tempered martensite with elongated subgrains and large density of dislocations inside the subgrains. On the boundaries of prior austenite grains, as well as the boundaries of subgrains, the $M_{23}C_6$ carbides were observed, while inside the subgrains – the precipitations of the MX type were disclosed.

Ageing of the examined cast steel contributed mostly to the privileged precipitation of $M_{23}C_6$ carbides on grain boundaries of former austenite grain. The number of precipitated $M_{23}C_6$ carbides on grain boundaries of former austenite grain was so large in some areas that they often formed the so-called continuous grid of precipitates (Fig. 5). Considerably less $M_{23}C_6$ carbides were noticed on the boundaries of polygonized ferrite (high-temperature tempered martensite). Greater intensification of the precipitation processes on grain boundaries of prior austenite grain compared to the grain boundaries of polygonized ferrite should be associated with the energy of these boundaries. The boundaries of prior austenite grains, as wide-angle boundaries, are characterized by higher energy of grain boundaries in comparison with the boundaries of polygonized ferrite grains which are narrow-angle boundaries of low energy.

Characteristic was also the observable diverse amount of carbides precipitated on particular boundaries of prior austenite grains – there were boundaries with a very large, as well as very small amount of carbides. Literature data indicate the influence of misorientation angle between the adjacent grains on the precipitation processes. Such an influence is also mentioned by Laws and Googhew [11] who have proved the interrelation between the quantity and size of chromium carbides precipitated on the boundaries and the type of boundaries and their misorientation angle in the austenitic stainless steels.

The morphology of each type of precipitates $M_{23}C_6$ and MX was the same as in the as – received state. However, the growth of precipitates of the $M_{23}C_6$ type was observed. The mean size of $M_{23}C_6$ carbides after ageing at the temperature of 550°C and time of 6000 hours ranged from 31 nm to 284 nm. Additionally, single large particles of ca. 433 nm were revealed. Whereas, for the ageing temperature of 600°C the range of $M_{23}C_6$ particle diameter varied from 25 to 377nm. An increase in the mean diameter of $M_{23}C_6$ carbides indicates the running process of coagulation of these precipitates which results from their pretty low thermodynamic stability which, according to [16], amounts to: – 20 kJ/mol. While in the case of precipitates of the MX type, this value amounts to: – 55 kJ/mol.

Probable increase in the mean diameter of $M_{23}C_6$ carbides during long term ageing of GP91 cast steel takes place by the mechanism of Ostwald ripening. The increase in the mean diameter of $M_{23}C_6$ carbides results in a decrease in the density number, because the volume fracture of $M_{23}C_6$ carbides is constant during Ostwald ripening. Therefore, the pinning effect of $M_{23}C_6$ carbides for the coarsening of laths decreases with time and it may have an effect on matrix polygonization. Abe et. al. [17] have show that for martensitic 9%Cr steels the stabilization of $M_{23}C_6$ carbides by the enrichment of boron contributes to a decrease in minimum creep rate and increase in the time to rupture.

Apart from the process of precipitation and coagulation of $M_{23}C_6$ carbides during ageing of the investigated cast steel there were processes of recovery and polygonization of the matrix running, which was revealed by a reduction in the dislocation density and increase in the subgrain width (Table 3).

Fig. 6 shows the mechanical properties of GP91 cast steel for the as – received condition and after ageing at 550 and 600°C for 6000 hours. As shown in the Fig. 6, the main results obtained in these tests revealed no degradation of the tensile properties (tensile strength and yield strength) on the aged material, comparing to as – received condition. Similar behaviour after thermal ageing treatments was also observed in the martensite steel [9]. In addition, it can be observed in the graphs that the time of ageing has no influence on these mechanical properties.

The GP91 cast steel showed a Vickers hardness value of 209 (±2) HV30 in as – received state. After ageing treatment (550 and 600°C for time 6000 h) this value did not change significantly – 198 (±3) and 196 (±2) HV30, respectively. The hardness results together with the microstructural stability observed can be considered the reason for the tensile behaviour of the GP91 cast steel after ageing. This indicates low ”sensitivity” of the strength properties to a decrease in strengthening by the dislocation and solution mechanism, and also implies mutual ”complementing” of the strengthening mechanisms. The effect of softening and matrix depletion of elements was compensated by the formation of fresh secondary particles $M_{23}C_6$, and possibly also by the Laves phase on grain boundaries.

According to calculations [19] the greatest increase in the yield strength in the case of high-chromium martensitic steels is connected with the refinement of microstructure with the boundaries of martensite laths. Strengthening by this mechanism constitutes ca. 33% of the total strengthening of martensitic steel, while for the dislocation and solution mechanism it amounts to 18 and 30%, respectively. Therefore, it is an extremely significant issue to increase the stability of $M_{23}C_6$ carbides or/and precipitations of Laves phase precipitated on the dislocation boundaries, effectively inhibiting the movement of dislocation boundaries, which allows to retain the lath substructure and slows down the processes of matrix polygonization.

TABLE 3

Parameters of subgrain microstructure in the as – received condition and after ageing of GP91 cast steel

Temperature, °C	**Ageing time, h**	**Mean diameter of subgrains, μm**	**Shape coefficient**	**Dislocation density 10^{14}m^{-2}**
as – received condition	—	0.708±0.258	0.701±0.151	2.95±2.02
550	6000	0.787±0.203	0.651±0.187	2.26±1.39
600	6000	0.748±0.321	0.705±0.154	2.22±1.23

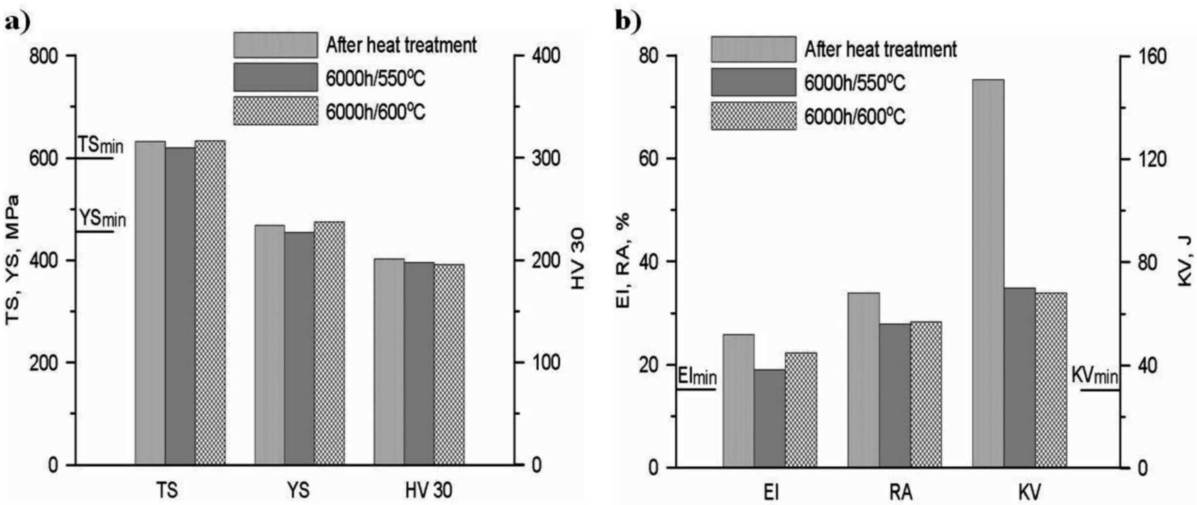

Fig. 6. Mechanical properties of GP91 cast steel for the as – received condition and after ageing at 550 and 600°C for times 6000 hours; a) strength properties; b) plastic properties

The strength properties comparable to the as-received condition were accompanied by a considerable decrease in impact strength KV from the level of 139 J in the as-received state, to the value of 70 J and 68 J after 6000 hrs of ageing at the respective temperatures of 550 and 600°C. Fall of the impact strength amounting to 50% undoubtedly was related to the privileged process of precipitation and coarsening (coagulation) of $M_{23}C_6$ carbides on the boundaries of prior austenite grain. Reduction in the impact strength of the examined cast steel was presumably influenced by the growth of subgrains. Literature data [20, 21] indicate also the possibility of decrease in the ductility of high-chromium steels as a result of enrichment of the near-boundary areas of grain boundaries in the atoms of impurities, e.g. atoms of phosphorus.

5. Summary

The GP91 on as – received condition is a fully martensite cast steel with fine grain size and 0.708±0.258 μm mean diameter of the subgrain. Two types of precipitates with different morphology have been observed in the cast steel, namely Cr rich carbides and Nb/V rich precipitates, indentified as $M_{23}C_6$ type, and MX (NbC, VX) type, respectively. The same precipitates have been detected in the aged condition of materials studied (550°C/6000h and 600°C/6000h). After ageing treatment a growth of $M_{23}C_6$ type carbides has been observed. Moreover, the processes of recovery and polygonization of the matrix could be noted, the effect of which was the growth of subgrain size and fall of the dislocation density. The above changes slightly influenced the strength properties of the examined cast steel, while the ageing resulted in a significant decrease in impact strength (by over 50%). This shows a crucial problem which is the stabilization of precipitates in steels/cast steels designed for long-term service at elevated temperatures.

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