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EFFECT OF DIFFERENT HEAT TREATMENTS ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF THE MARTENSITIC GX12CrMoVNbN9-1 CAST STEEL

WPŁYW PARAMETRÓW OBRÓBKI CIEPLNEJ NA MIKROSTRUKTURĘ I WŁAŚCIWOŚCI MECHANICZNE MARTENZYTYCZNEGO STALIWA GX12CrMoVNbN9-1

The paper presents a research on the influence of multistage heat treatment with the assumed parameters of temperature and time on the microstructure and mechanical properties of high-chromium martensitic GX12CrMoVNbN9-1 (GP91) cast steel. In the as-cast state GP91 cast steel was characterized by a microstructure of lath martensite with numerous precipitations of carbides of the $M_{23}C_6$, M_3C and NbC type, with its properties higher than the required minimum. Hardening of the examined cast steel contributes to obtaining a microstructure of partly auto-tempered martensite of very high strength properties and impact strength KV on the level of 9÷15 J. Quenching and tempering with subsequent stress relief annealing of GP91 cast steel contributed to obtaining the microstructure of high-tempered lath martensite with numerous precipitations of the $M_{23}C_6$ and MX type of diverse size. The microstructure of GP91 cast steel received after heat treatment was characterized by strength properties (yield strength, tensile strength) higher than the required minimum and a very high impact energy KV. It has been proved that GP91 cast steel subject to heat treatment No. 2 as a result of two-time heating above the Ac_3 temperature is characterized by the highest impact energy.

Keywords: heat treatment, microstructure, mechanical properties, GP91 cast steel

W pracy przedstawiono badania wpływu wieloetapowej obróbki cieplnej przy założonych parametrach temperaturowo – czasowych na mikrostrukturę i właściwości mechaniczne wysokochromowego, martenzytycznego staliwa GX12CrMoVNbN9-1 (GP91). W stanie lanym staliwo GP91 charakteryzowało się mikrostrukturą martenzytu listwowego z licznymi wydzieleniami węglików typu $M_{23}C_6$, M_3C i NbC o właściwościach wyższych od wymaganego minimum. Hartowanie badanego staliwa przyczynia się do uzyskania mikrostruktury częściowo samoodpuszczonego martenzytu, o bardzo wysokich właściwościach wytrzymałościowych i udarności KV na poziomie 9÷15 J. Ulepszanie cieplne z następnym wyżarzaniem odprężającym staliwa GP91 przyczyniła się do uzyskania mikrostruktury listwowego martenzytu wysokoodpuszczonego, z licznymi, o zróżnicowanej wielkości wydzieleniami typu $M_{23}C_6$ i MX . Uzyskana drogą obróbki cieplnej mikrostruktura staliwa GP91 charakteryzowała się właściwościami wytrzymałościowymi (granicą plastyczności, wytrzymałością na rozciąganie) wyższymi od wymaganego minimum i bardzo wysoka udarnością KV. Wykazano, że staliwo GP91 poddane obróbce No. 2 w wyniku dwukrotnego nagrzewania powyżej temperatury Ac_3 charakteryzuje się najwyższą udarnością.

1. Introduction

Limitations connected with the emission of pollutants into the atmosphere and aiming to increase the efficiency of power units have contributed to the development of high-temperature creep resisting steels. Under many research projects a number of new steel grades have been developed and introduced into the power industry, widely called martensitic and bainitic steels, such as: P91, P92, T24, T23. These steels were worked out as a result of modification in the chemical composition and optimization of microstructure of the steels previously applied in the power industry [1-3]. Apart from the above-mentioned steel grades, characterized by higher properties compared to the low-alloy steels used so far, and high-chromium X20CrMoV121 steel, it was necessary to introduce new grades of cast steel. Cast steels play a key role as turbine components such as: cylinders and casings of turbines, valve chambers, T-pipes etc. The requirements set for newly implemented high-chromium martensitic cast steels were high, i.e.: 100 000 hrs creep strength of 100 MPa at 600°C, good castability and weldability, properties such as fracture toughness, low – cycle fatigue strength and long – term toughness, corresponding at least to those of the low – alloys, ferritic cast steels currently used up to 565°C and through – hardening capability up to about 500 mm wall thickness [4, 5]. One of the new grades of casting materials is GX12CrMoVNbN9-1 (GP91) cast steel. The cast steel was worked out on the basis of chemical composition of P91 steel, therefore the microstruc-

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tures as well as required mechanical properties of these materials are similar. Forming of the microstructure and mechanical properties of cast steels takes place through heat treatment. Steel castings used in the power industry due to their dimensions are subject to long-term multi-stage treatment. It is the heat treatment that determines further stability of the cast steel microstructure and properties during its long-term service at elevated temperature [6, 7]. The aim of the performed research was to assess the influence of multi-stage heat treatment with the assumed parameters of temperature and time on the microstructure and mechanical properties of high-chromium martensitic GX12CrMoVNbN9-1 cast steel.

2. Methodology of research

The microstructural research was carried out by means of Axiovert 25 optical microscopy (OM) on metallographic specimens prepared conventionally, etched with ferric chloride, and by means of JOEL JEM – 3010 high – resolution transmission electron microscope (TEM) using thin foils. Identification of precipitates was made by means of thin foils and extraction carbon replicas. The tests were carried out on test samples in the as-cast state and after heat treatment with the assumed parameters of temperature and time. Static test of tension was run by means of MTS – 810 testing machine. Measurement of hardness was made using the Vickers method with the indenter load of 30kG (294,2N) by means of Future – Tech FV – 700 hardness tester. The tests of impact energy were run on standard V-notched bar test pieces. As far as the static tensile test and hardness measurement is concerned, the presented results are the average of three tests, while the value of hardness is the average of five measurements.

3. Research results and their analysis

3.1. Material for research

The material of study was GX12CrMoVNbN9-1 (GP91) cast steel of the following chemical composition (%mass): 0.12C, 0.49Mn, 0.31Si, 0.014P, 0.004S, 8.22Cr, 0.90Mo, 0.12V, 0.07Nb, 0.04N.

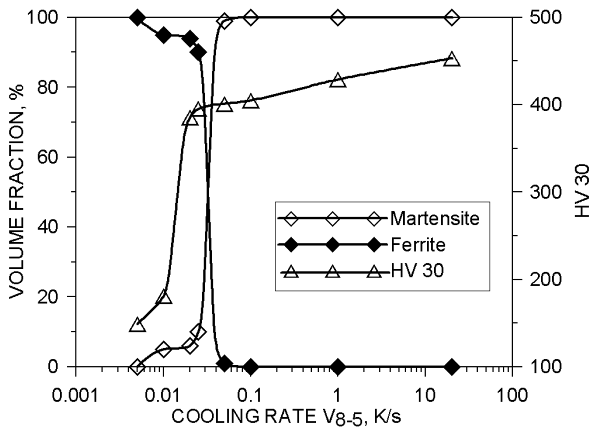

Fig. 1. Influence of cooling rate on the microstructure and hardness of GP91 cast steel [8]

The content of chromium of above 8%, an addition of molybdenum of about 1% and microadditions of vanadium and niobium ensure good hardenability of the examined cast steel. Transformation of super-cooled austenite into martensite in the investigated cast steel runs at the rates higher than ca. 2°C/min. Slower cooling contributes to the occurrence of microstructure composed of ferrite and carbide precipitates (Fig. 1). Good hardenability of the examined cast steel allows air hardening of intersections of 80-100 mm width. The casts with larger intersections require faster cooling from the austenitizing temperature; in modern foundries the polymers are used for cooling, while in traditional ones the cooling agent is still oil [9, 10].

3.2. Microstructure and properties of GP91 cast steel in the as – cast state

High hardenability of the investigated cast steel and its coarse grained structure in the as-cast state made it possible to obtain martensitic microstructure with numerous precipitations of diverse morphology (Fig. 2). Apart from the lath martensite with large dislocation density observed in the microstructure of the examined cast steel there was also a polygonal substructure noticed (Fig. 2). The width of martensite laths in the as-cast state amounted to ca. 0.30÷0.45 μm. Precipitations in the cast steel microstructure in the as-cast condition were seen on the boundaries of laths and subgrains as well as inside the laths. (Fig. 2b).

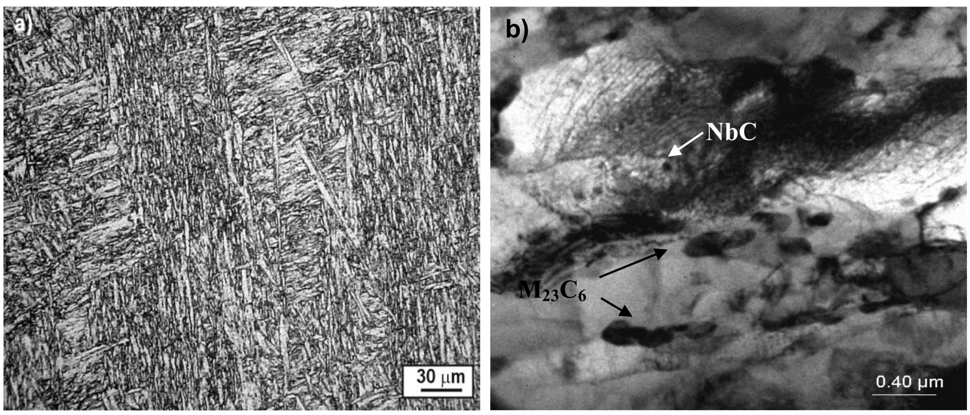

Fig. 2. Microstructure of GP91 cast steel in the as-cast state: a) OM, b) TEM, thin foil

Performed identification of precipitates in GP91 cast steel in the as-cast condition revealed the presence of three precipitation types:

√ large chromium-rich $M_{23}C_6$ precipitates of about 100÷350 nm, precipitated mostly on the boundaries of prior austenite grains and martensite laths (Fig. 2, 3);
√ fine-dispersive spherical NbC carbides precipitated not only on the dislocations inside martensite laths, but also on the boundaries of subgrains (Fig. 2);
√ lamellar M_3C carbides precipitated in the Widmannstätten pattern (Fig. 3).

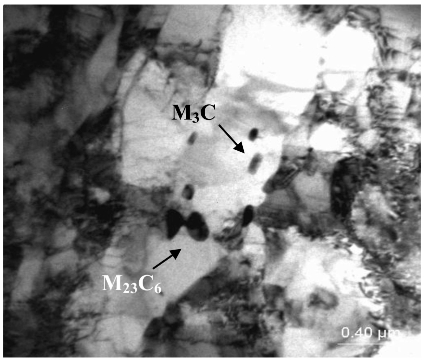

Fig. 3. The effects of auto-tempering of martensite in GP91 cast steel in the as-cast state

Mechanical properties of GP91 cast steel in the as-cast state are included in Table 1. Tensile strength and yield strength determined for GP91 cast steel in the as-cast state were higher than the required minimum by ca. 10%. Plastic properties, i.e. impact energy and elongation were higher respectively: over 3 – times and by around 33% than the required minimum. Hardness of the examined cast steel in the as-cast condition amounted to 232HV30, whilst the percentage reduction of area – 58% (Table 1).

TABLE 1

Mechanical properties of GP91 cast steel in the as-cast state

	TS MPa	YS MPa	El. %	RA %	KV J	HV30
as-cast state	644	506	20	58	94	232
requirements according to [12]	min. 600	min. 450	min. 15	–	min. 30	–

The required mechanical properties in the as-cast condition (Table 1) is what GP91 cast steel most of all owes to the lath microstructure of low-carbon martensite (Fig. 2). High temperature at the beginning of martensite transformation M_s, amounting to 386°C, may indicate the effect of auto-tempering of martensite microstructure in the investigated cast steel. The coarse grained cast structure of GP91 cast steel, unfavorable from the point of view of properties, undergoes a refinement with martensite laths. This leads to the growth of strengthening with grain boundaries, which is beneficial for both: plastic properties as well as strength properties. According to literature data [11], strengthening with grain boundaries in the case of martensitic structure is dependent on the width of martensite laths and for the width of ca. 0.36 μm (similar to that of examined cast steel) amounts to 239.4MPa, and may constitute ca. 33% of total strengthening in 9-12%Cr steels/cast steels.

3.3. Microstructure and properties of GP91 cast steel in the hardened state

After hardening the investigated cast steel was characterized by the microstructure of lath martensite with noticeable effects of partial auto-tempering (Fig. 4). High temperature M_s=386°C enables the diffusion of carbon which favors the precipitation of M_3C carbides inside martensite laths already while cooling. According to the data [13], M_3C carbide can precipitate in the steel just after ca. 0.29s at the temperature of 690°C. In the microstructure of hardened cast steel apart from M_3C carbides also the NbC precipitates could be seen.

The NbC (NbX) carbides (carbonitrides) of niobium, precipitating in the final phase of coagulation, are an inhibiting factor for the austenite grain growth, which has a favorable influence on further properties of the alloy.

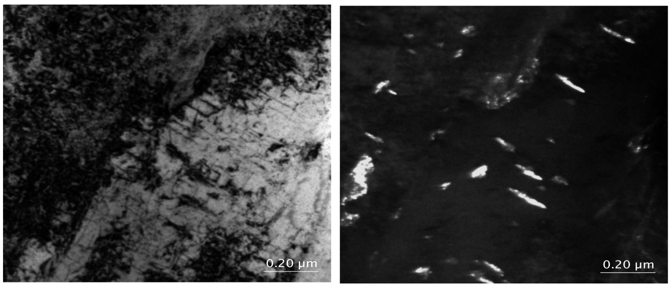

Fig. 4. Microstructure of GP91 cast steel after hardening, TEM, thin foil

As proved by the tests carried out by means of THERMO-CALC program, the MX precipitates in the investigated cast steel may remain stable even to the austenitizing temperature of about 1345K [14]. According to literature data [15], the primary precipitates rich in niobium may also be the cause of an increase in their brittleness connected with formation of the so-called stony fractures. Particles of ε – carbide were not found in the microstructure of state No. 3. However, their occurrence in auto-tempered martensite of 9%Cr steel has been reported by Brühl et al [16] and Soraja et al. [17].

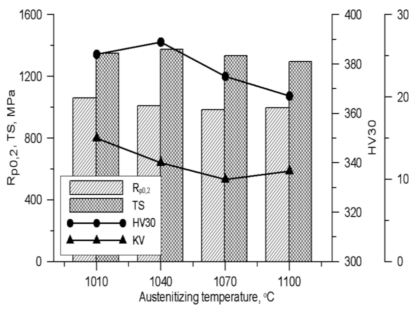

Fig. 5. Influence of austenitizing temperature on mechanical properties of GP91 cast steel after hardening process

The influence of austenitizing temperature on mechanical properties of GP91 cast steel in the hardened condition is presented in Fig. 5. The cast steel was characterized by very high strength properties – $R_{p0,2}$ ≈1000 MPa, R_m ≈1300 MPa, hardness of 380 HV30. The maximum strength properties were achieved in the cast steel after hardening from the austenitizing temperature of 1010 and 1040°C. Austenitizing at the temperature above 1040°C causes a reduction in the strength properties. It probably results from the enrichment of austenite in alloy elements as a consequence of dissolution of carbide phases and the related increase of retained austenite volume fraction in the examined cast steel in the hardened condition. The decline of strength properties is also influenced significantly by the observed beginning of austenite grain growth at the austenitizing temperature of 1100°C Impact energy KV of the examined cast steel depending on the temperature of austenitizing was on the level of 9÷15 J.

3.4. Heat treatment of GX12CrMoVNbN9-1 (GP91) cast steel

The heat treatment parameters for GP91 cast steel are included in Table 2. The temperature – time parameters of heat treatment gathered from works [5-7, 21-22], are applied in industry for the treatment of multi-ton large-size steel castings.

TABLE 2
Temperature – time parameters of heat treatment for GP91 cast steel

Heat treatment	Temperature – time parameters of heat treatment for GP91 cast steel	Ref.
No. 1	780°C/8h/furnace + 1090°C/12h/air + 730°C/8h/ air + 730°C/8h/ furnace	[5]
No. 2	1000°C/15/ furnace + 1100°C/12h/ air + 730°C/12h/ air + 730°C/12h/ furnace	[6]
No. 3	1040°C/12h/ air + 760°C/12h/ air + 750°C/8h/ furnace	[7]

Last steps at 730 (heat treatment No. 1 and No. 2) and 750°C (heat treatment No. 3) were given to simulate a Post Weld Heat Treatment (PWHT).

3.5. Microstructure and properties of GP91 cast steel after heat treatment

High temperature of austenitizing above 1000°C is necessary in order to dissolve most of the precipitates in the matrix. This ensures the matrix saturation with alloy elements and provides the required hardenability. However, part of the precipitates, mostly NbC (NbX), remain undissolved, inhibiting the grain growth during the process of austenitization. The applied parameters of heat treatment of GP91 cast steel (Table 2) contributed to obtaining fine-grained microstructure of high-tempered martensite. The mean diameter of austenite grain received after heat treatment No. 1 and No. 3 amounted to ca. 25 μm, which corresponds to the grain size – 8, according to ASTM. Examples of microstructures of GP91 cast steel after heat treatment are illustrated in Fig. 6. In the case of heat treatment No. 2 as a result of two-time heating of the examined cast steel above the temperature A_{c1} (A_{c3}), a greater refinement of microstructure was observed in comparison with the cast steels subject to one-time heating only. In this case the mean diameter of grain amounted to 13.6 μm, which corresponds to the grain size grade No. 9. Grain size reduction has a favourable effect on mechanical properties of the cast steel in two opposite directions: at the same time raises the yield strength and impact strength and decreases the nil ductility transition temperature. High initial value of impact strength of materials designed for long-term service at elevated temperature is necessary, since, as literature data show [18, 19], during operation the decreasing of impact strength proceeds faster compared to the strength properties. High temperature and long holding times at the temperature of tempering/annealing result in the precipitation of numerous carbides of diverse size. The carbides precipitates were observed not only on the boundaries of prior austenite grain, but also on the boundaries of martensite laths, and inside martensite grains.

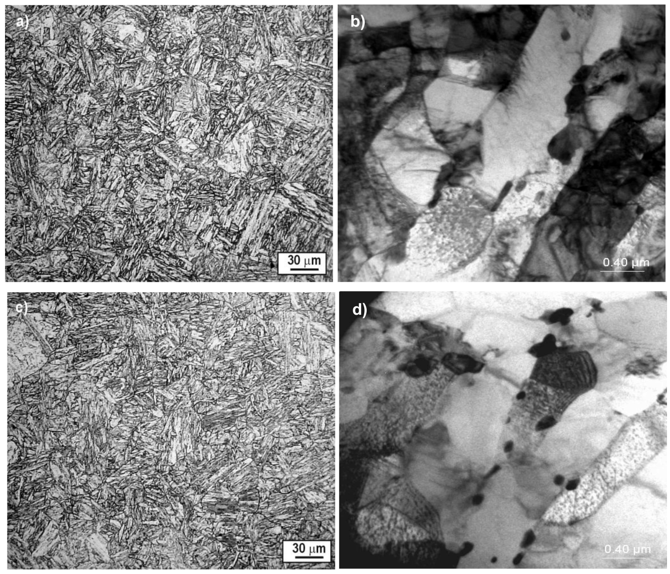

Fig. 6. Microstructure of GP91 cast steel after heat treatment: a, b) treatment No. 1; c, d) treatment No. 2; OM (a, c), TEM (b, d) – thin foil

Lengthy holding during tempering and stress relief annealing (PWHT) is essential in order to obtain a very stable microstructure. As practice shows, the higher the temperature of tempering/ annealing of the cast steel, the more stable the microstructure of the casts during service at elevated temperature.

Microstructures of GP91 cast steel after various heat treatment options were similar and characterized by a lath substructure of martensite with large dislocation density and polygonal grains of ferrite. Between martensite laths, as well as subgrains, the dislocation boundaries occurred. The estimated density of dislocations in the examined cast steel amounted to ca. $2 \div 5 \cdot 10^{14}$ m^{-2}. Performed identifications of precipitates in the cast steel after heat treatment revealed the presence of $M_{23}C_6$ and MX carbides in the microstructure. Large number of $M_{23}C_6$ carbides occurred mostly on the boundaries of prior austenite and on the boundaries of subgrains/ laths of martensite. Only some sparse carbides of this type were seen also inside ferrite subgrains. The size of precipitated $M_{23}C_6$ carbides was diverse and ranged from ca. 60 nm to over 210 nm. Fine-dispersive 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 revealed, 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.

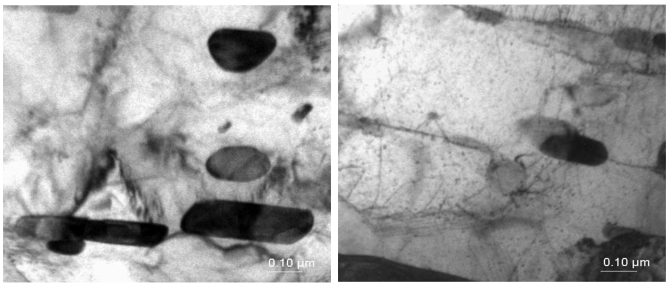

Fig. 7. Morphology of precipitates in GP91 cast steel after heat treatment No. 3

The V-rich MX particles which were found in the microstructure after tempering evidently precipitated 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 carbides of $M_{23}C_6$ revealed in the microstructure, precipitated on the boundaries of martensite subgrains/laths, stabilize the subgrain miocrostructure of martensite inhibiting the movement of dislocation boundaries, whilst the fine-dispersive precipitates of MX provide high creep resistance by inhibiting the dislocation movement. Figure 7 presents examples of morphologies of precipitations in the investigated cast steel. Detailed description of precipitation processes in the given cast steel is included in work [20].

Figure 8 includes the results of research on mechanical properties of GP91 after the applied variants of heat treatment.

The research carried out on mechanical properties of GP91 cast steel after heat treatment in accordance with the variants included in Table 2 has proved that:

- the strength properties – yield strength and tensile strength, in spite of many hours of holding at the tempering/annealing temperature which caused their decrease in comparison with the hardened state by more than 50%, fulfill the minimum requirements. According to literature data [6], extending the time of tempering at the temperature of 730°C from five to twenty-five hours contributes to a decrease in the yield strength and tensile strength of the high-chromium cast steel by around 12 and 4%, respectively. In spite of the above, tempering (or/ and annealing) the steel casts for many hours at the temperature above 700°C is necessary in order to provide the maximum high thermodynamically stable microstructure;
- austenite grain size reduction as a consequence of the austenitizing process and fall of the matrix strengthening results in the growth of plastic properties, particularly impact energy of the examined cast steel (Fig. 5). In the case of heat treatment No. 2 it is easy to notice the positive effect of two-time reduction in grain size on the growth of yield strength and impact strength, compared to other variants of heat treatment.
- hardness of GP91 cast steel after heat treatment for the analyzed cases was higher than 200HV30, which proves high stability of microstructure of the examined alloy.

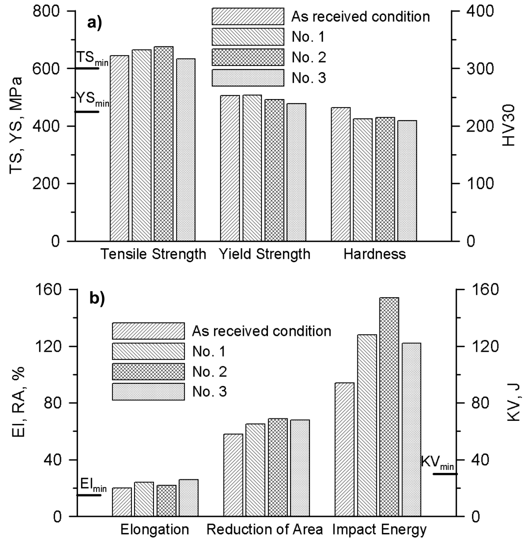

Fig. 8. Comparing: a) strength properties, b) plastic properties of GP91 cast steel in the as-cast condition and after heat treatment

4. Conclusions

1. The GP91 cast steel having a coarse grained structure in the as-cast condition is characterized by high mechanical properties which result from the lath microstructure of low-carbon martensite. High properties of GP91 cast steel in the as-cast state indicate a dominant role that the dislocation boundaries between martensite laths play in the mechanism of strengthening, and a slight contribution of wide-angle boundaries of prior austenite grain for this mechanism.
2. High strength properties of the examined cast steel are provided by hardening within the temperature range of 1010-1040°C. Higher temperatures of austenitizing lead to the reduction of strength properties in the hardened state.
3. Heat treatment of GP91 cast steel contributed to the growth of plastic properties, mostly impact energy. The strength properties in spite of long holding times at the temperatures of tempering/ annealing, necessary for high-temperature creep resisting materials, were higher than the required minimum. This proves high stability of microstructure of the examined cast steel.

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