INFLUENCE OF MODIFICATION ON THE CHARACTERISTICS OF REINFORCING STEELS INTENDED FOR REINFORCED CONCRETE STRUCTURES

We review and analyse the reasons of destabilizing the chemical composition and mechanical characteristics reinforcing low-carbon steels and present ways to solve these problems. As determined, both the instability of the chemical composition and the non-metallic inclusions of an elongated and acute-angled shape, containing an excessive amount of gas and other impurities, reduce the service life of the finished metallurgical product and lead to a deterioration in the quality of the finished product. As established and proven, one of the ways to maximize the chemical-composition stabilization and to improve mechanical characteristics, as well as the quality of the reinforcement, is the steel-melts’ processing with multifunctional-action modifiers. As determined, the St1kp steel, like other low-alloy steels, is a multicomponent system consisting of 17 or more components. Each of the impurities, as well as deoxidizing modifier elements (Al, Ti, Mg), can change significantly the composition of non-metallic inclusions, the main matrix, cementite, grain size, mechanical characteristics, and their stability. As established, after modification, the St1kp-steel grain structure is almost 2 times finer, after which it can be asserted safely that such a material can last longer. As revealed, all mechanical-characteristics’ parameters of the modified metal met the requirements of the State Standards (DSTU) 2770-94 and exceed the serial ones. This is especially important for reinforced concrete structures, since the insufficient level of mechanical characteristics and their instability cannot guarantee the reliability and durability of their operation. As noted, during the solidification of the modified ingot, mainly volumetric crystallization takes place, and not heat-sink-oriented crystallization, as for serial metal.

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The predominant mechanism of bulk crystallization is one of the main reasons for the stabilization of the chemical composition and the increase in the mechanical-characteristics' level of steels under the complex influence of alloying components and harmful impurities of steel both serial and modified with multifunctional modifiers of melts. As proved in the work, after modification, the morphology of non-metallic inclusions is significantly improved. As a result, the quality of the finished reinforcement is significantly increased.

Keywords: fittings, St1kp steel, modifiers of multifunctional action, chemical and phase compositions, structure, dislocation density, mechanical characteristics, non-metallic inclusions.

1. Introduction

Contemporary iron–carbon alloys are multicomponent native complex systems due to the ingress of scrap and waste from various other alloys, such as sulphur, phosphorus and arsenic, during their smelting, which, as a result, causes destabilization of the chemical composition and mechanical characteristics. As a result, it is difficult to predict the service life of a finished steel product since such events lead to deterioration in the quality of the finished product. Under specific conditions to produce reinforcing steel at low-section mills of open joint-stock company (OJSC) 'ArcelorMittal Kryvyi Rih', the temperature of the end of the rolled product changes in the range of 1050–1100 °C, which, according to Ref. [1], causes a change in the tensile strength, and the strength of the reinforcement varies due to fluctuations in the temperature of the cooling water during heat treatment. According to expert assessment, a change in strength (within 200 MPa) also causes a fluctuation in the size of the profile due to wear of the calibres and the associated change in the rolling speed (duration of forced cooling). A more significant (up to 100–120 N/mm²) fluctuation of strength values due to a decrease in the duration of cooling (at a constant length of installations) is associated with the acceleration of the movement of the rolls after leaving the mill stand (increased speed of the roller table and acceleration in the cooling installation). Thus, the maximum total change in the strength of heat-treated rolled products due to these factors can be up to 160 MPa under unfavourable conditions.

The performed studies [2] of the chemical inhomogeneity of steel and the mechanical properties of hardened reinforcement make it possible to assess the influence of this factor on the level of properties of the finished rolled metal.

The chemical inhomogeneity of a rebar billet rolled from an ingot weighing 12.5 tons is determined by the spectral method by the cross-section of templates (in the centre, at 1/4 of the diagonal and in the corner) with an arc discharge ‘spot’ diameter of 6 mm, and rebar — by
chemical analysis chips selected according to the cross section of the profile on similar horizons of ingots rolling. Such reinforcement is the basis for the creation of reinforced concrete structures used in building products.

Reinforced concrete is one of the most used building materials in construction today. Structures made of this material are highly durable and suitable for almost any design solutions. Building elements of buildings and structures made of reinforced concrete, in comparison with steel structures, have high fire resistance. The existing regulatory documentation and the work of many scientists studying the behaviour of reinforced concrete structures under conditions of thermal exposure from a fire presented a variety of methods describing the operation of these structures under these conditions [3].

The load-bearing structures of modern buildings are made of reinforced concrete. Comparing with other building materials, which are used for the installation of critical structures, reinforced concrete is in the lead. The advantages of this material are high strength, durability, high fire resistance, which makes this material the most in demand. One of the main aspects of ensuring fire safety in the design or operation of existing buildings and structures is the use of building structures with guaranteed fire resistance classes. Compliance of structures with the required fire resistance classes allows for the safe evacuation of people in case of fire and provides an opportunity to carry out effectively rescue work for special units. In addition, reinforcement should have a high level of corrosion resistance, deformability, a high level of plasticity in combination with optimal strength and meet other requirements number [4].

Reliability is the property of a structure to perform specified functions while maintaining its performance within specified limits for the required period or the required operating time [5]. This important indicator includes the reliability, durability, storability, and maintainability of the structure as a whole and its structures.

Reliability is the property of an object to maintain continuously operability during a specified service life. Reliability indicators include the probability of failure-free operation, mean time to first failure, failure rate, failure rate parameter, warranty time.

Durability is the property of an object to remain operational until the limit state occurs with the necessary breaks for maintenance and repairs. Longevity indicators are the average service life, service life until the first overhaul, service life between repairs. Thus, reliability and durability are the properties of an object to maintain operability, while reliability provides for continuous operability for a certain time and durability with possible breaks for repairs.

Persistence is the property of an object to maintain continuously a healthy and operable state. It includes the ability of a structure to with-
stand the negative effects of poor storage and transportation, and the persistence of the facility as a whole, prior to commissioning and during repairs.

Maintainability is the availability of an object in carrying out measures to prevent and detect the causes of failures and damages, as well as to eliminate them through repair and maintenance. Maintainability indicators include the probability of recovery at a given time, the average recovery time, the specific labour intensity of maintenance and repairs, the average cost of repairs.

In the process of designing an object, its theoretical reliability is laid. During the construction process, the actual reliability of each element is ensured, which depends on the quality of assembly and installation of structures made of appropriate materials. Further, reliability must be maintained at the required level by the correct operation of the facility.

During operation, the reliability of the bridge structure is affected by the following conditions: internal stresses in the structure that do not correspond to their design values, external influences, the system of maintenance and repairs.

All factors causing changes in the performance of the bridge structure as a whole and individual elements can be divided into two groups of reasons: internal and external.

Internal reasons include:
- physical and chemical processes occurring in the materials from which structures were made;
- loads and processes arising during operation;
- constructive factors;
- manufacturing quality.

External causes include:
- climatic factors: temperature, humidity, solar radiation;
- environmental factors: wind, dust, sand, the presence of aggressive compounds in the atmosphere, biological factors;
- quality of operation;
- maintenance and repair.

Therefore, levelling the above factors and obtaining the optimal level of mechanical characteristics are one of the main tasks of modern metallurgy. Along with increasing requirements for strength characteristics, it is very often necessary not only to maintain, but also to increase the level of mechanical characteristics of structural steel. This concerns the tendency of steel to brittle fractures; then, construction, industry and transport require structural steels with a cold brittleness threshold of \( \leq 60 ^\circ \text{C} \) in samples with the most severe sharp notch (KCV-60) [6].

The operational requirements also include good weldability, high corrosion and fatigue resistance, etc. Today, for these purposes, chromium,
nickel, molybdenum, vanadium, niobium, etc. are added to the composition of steel. Ferrite, the main contribution to which is made by multifunctional modifiers, regulates the grain microstructure of the metal. In this case, the dispersion and amount of this excess phase is determined not so much by the level of concentrations and the ratio of phase-forming elements (vanadium and nitrogen), but by the temperature conditions of rolling and subsequent heat treatment, since during hot deformation of reinforcing steels, vanadium carbonitrides disproportionate and all nitrogen is in solid solution. In terms of heat treatment, this provision also applies to cast metal products since the formation of vanadium nitrides occurs after steel crystallization or during cooling of the casting after temperature–time effects (normalization or quenching and tempering).

Considering the high cost and scarcity of vanadium and its alloys for the Ukrainian industry, the main direction for improving the mechanical properties and performance characteristics of structural steels of the ferrite–pearlitic class is the implementation of carbonitride hardening (CNU) processes based on cheaper and more accessible metals, namely titanium, magnesium and aluminium. As modern practice shows, one of the ways to maximize the stabilization of the chemical composition and improve the mechanical characteristics is the treatment of steel melts with modifiers of multifunctional action [7, 8].

The competitiveness and demand for metal products in the world market depends on the level of mechanical characteristics of the finished product. However, the question of substantiating the choice of the composition of deoxidizers–modifiers of multifunctional action in the processing of metal in a ladle, their optimal concentration and the moment of introduction, and the selection of rational evacuation modes, which will provide the required carbon content and minimize the content of non-metallic inclusions and obtain the optimal structure, remains open one of the priority and difficult tasks of metallurgy [9].

Therefore, it became necessary to conduct such tests. For this, St1kp steel was smelted in 160-ton converters at an oxygen consumption of 380 m³/min and a blowing time of 22 minutes, after blowing, 21 minutes and a melt temperature of 1605–1610 °C. During melting, a mixture was introduced into the converter, consisting of scrap metal, liquid iron (1330 °C), SiMn, FeMn, and anthracite. The melt temperature of steel St1kp in the converter before deoxidation and inoculation was of 1630–1660 °C. During the melting process, an express analysis of the content of C, Mn, S, and P was carried out. The materials for producing low-carbon steel were, liquid pig iron, scrap steel, iron ore, slag lime, slag liquefaction bauxite, slag liquefaction fluorspar, SiMn, FeMn, heavy aluminium (30%), anthracite. FeTi is also used to increase the yield. Ferroalloys, deoxidizers–modifiers were added to the melt in the above
sequence. The disadvantage of such deoxidizers–modifiers–ligatures is their incomplete assimilation by melts, because of which the instability of mechanical characteristics is obtained. This reduces the service life of finished metal products. Even though research in the field of modifying steels and alloys is carried out today by many specialists, this topic remains relevant [10–12].

In this regard, in this article, we analyse the effect of multifunctional modifiers on the characteristics of reinforcing steels on their characteristics for use in building structures.

2. Experimental and Theoretical Details

The chemical composition of steels St1kp and St3ps, according to DSTU 2770-94, includes the main alloying elements C, Mn, Si, which determine the level of strength and ductility of the final product. At the same time, there are several accompanying elements in steel, for example, Cr, Ni, Cu, As, B, Mo, V, Ti, Zn, Sb, Sn, Bi, B, Pb, Cd, etc., which fall into it due to the use of non-regulated chemical composition scrap in the smelting of steel, ferroalloys and ore. Therefore, St1kp steel, like other low-alloy steels, is a multicomponent system consisting of 17 or more components, considering harmful impurities (S and P), gases (O, N, H) and heavy elements Zn, Sb, Sn, Bi, B, Pb, Cd, etc. Therefore, the composition of St1kp steel at OJSC ‘ArcelorMittal Kryvyi Rih’ is controlled by 15 elements, and not by 10, as according to DSTU. Each of the impurities, as well as deoxidizing modifier elements (Al, Ti, Mg, Mn, C) can significantly change the composition of non-metallic inclusions, the main matrix, cementite, grain size, mechanical characteristics and their stability [13].

In connection with the above, OJSC ‘ArcelorMittal Kryvyi Rih’ conducted a pilot-industrial melting with the use of multifunctional modifiers. After the smelting of this reinforcing structural steel, data on the chemical composition, structure, non-metallic inclusions and mechanical characteristics were obtained and processed. Thanks to them, it was possible to determine why the quality of serial metal is not enough. Its chemical composition is presented in Table. 1.

Table 1. Steel St1kp and St3ps chemical composition according to DSTU 2770-94 [15, 21]

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Mass fraction of chemical elements, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>St1kp</td>
<td>0.06–0.12</td>
</tr>
<tr>
<td>St3gsp</td>
<td>0.14–0.22</td>
</tr>
</tbody>
</table>
3. Results and Discussion

3.1. Chemical Composition of St1kp Wheel Steel

Studies of a large array of statistical data for commercial steel St1kp showed that in metallurgical production there is a large range (difference between max and min) of the content of alloying elements both within the same heat and between heats [7]. This is due to several factors: large volumes of molten metal in ladles, the multicomponent composition of modern steels, the introduction of impurities not only from iron-containing charge, but also from ligatures, ore, ferroalloys, deoxidizers, refractories, violation of technological discipline, wide tolerances for the content of elements according to technical documentation.

According to DSTU 2770-94, the range of content of all alloying (C, Mn, Si), microalloying elements (Cr, Ni, Cu, Mo, V) and harmful impurities is within a wide range. So, according to the DSTU data (Table 2), the sum of alloying elements is 0.67% wt., the maximum amount of Cr + Ni + Cu = 0.9% wt. and the largest amount S + P = 0.09% wt. At the same time, the minimum the sum of alloying elements is 0.31% wt., and the minimum sum of Cr + Ni + Cu and S + P is 0% wt. Consequently, even zero content of some components is allowed, and the maximum number of alloying elements differs from the minimum by more than 2 times, which can significantly change the inter melting composition of St1kp reinforcing steel, which is used for a special purpose. By processing the array of statistical data of 34 serial heats (Table 2, 160 tons each), it was determined that the difference (max − min) of the inter melt content of each element was noticeable: C — 0.05 wt.%, Mn — 0.24 wt.%; Si — 0.04 wt.%; S — 0.022 wt.%; P — 0.010 wt.%, Cr — 0.05 wt.%, Ni — 0.06% wt.%, and Cu — 0.06 wt.% [14].

The concentration range (max−min) in serial melts, control in relation to modified ones, is calculated with statistical processing of the results shown in Table 2. Since nickel, copper, and chromium come as random components of steel from scrap (stainless steel waste with an increased amount of Cr, Ni and Cu comes from scrap electrical, electronic and household appliances), it is practically difficult to change the situation. However, when the difference between the melting composition is equal to 0.04 wt.% for Si, 0.05 wt.% for C, 0.24 wt.% for Mn as main alloying elements, and 0.022% for P, 0.01% for S, 0.003% for N as impurities, this is a significant argument against the use of such a metal for a special purpose (manufacturing of reinforced concrete structures).

Therefore, it became necessary to change significantly the technology of smelting St1kp steel to stabilize the chemical composition of both the main alloying elements and harmful impurities. At the metal-
Table 2. Average statistical data of industrial heats of mild steel St1kp (34 serial heats and 17 modified heats) [13, 15]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>N</th>
<th>As</th>
<th>Ti</th>
<th>B</th>
<th>Mo</th>
<th>V</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Serial metal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average meaning</td>
<td>0.08</td>
<td>0.39</td>
<td>0.05</td>
<td>0.022</td>
<td>0.015</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
<td>0.007</td>
<td>0.005</td>
<td>0.005</td>
<td>0.008</td>
<td>0.008</td>
<td>0.005</td>
<td>0</td>
</tr>
<tr>
<td>Coefficient variations</td>
<td>0.15</td>
<td>0.10</td>
<td>0.26</td>
<td>0.265</td>
<td>0.327</td>
<td>0.31</td>
<td>0.55</td>
<td>0.42</td>
<td>0.161</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.001</td>
<td>0</td>
</tr>
<tr>
<td>Maximum meaning</td>
<td>0.10</td>
<td>0.49</td>
<td>0.05</td>
<td>0.037</td>
<td>0.015</td>
<td>0.07</td>
<td>0.07</td>
<td>0.08</td>
<td>0.008</td>
<td>0.005</td>
<td>0.005</td>
<td>0.008</td>
<td>0.008</td>
<td>0.005</td>
<td>0</td>
</tr>
<tr>
<td>Minimum meaning</td>
<td>0.05</td>
<td>0.25</td>
<td>0.01</td>
<td>0.015</td>
<td>0.005</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.008</td>
<td>0.008</td>
<td>0.003</td>
<td>0</td>
</tr>
<tr>
<td>Difference</td>
<td>0.05</td>
<td>0.24</td>
<td>0.04</td>
<td>0.022</td>
<td>0.010</td>
<td>0.05</td>
<td>0.06</td>
<td>0.06</td>
<td>0.003</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.002</td>
<td>0</td>
</tr>
<tr>
<td><strong>Modified</strong></td>
<td></td>
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<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average meaning</td>
<td>0.085</td>
<td>0.40</td>
<td>0.03</td>
<td>0.019</td>
<td>0.008</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
<td>0.006</td>
<td>0.005</td>
<td>0.005</td>
<td>0.008</td>
<td>0.008</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>Coefficient variations</td>
<td>0.11</td>
<td>0.06</td>
<td>0.23</td>
<td>0.158</td>
<td>0.198</td>
<td>0.18</td>
<td>0.20</td>
<td>0.28</td>
<td>0.118</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.10</td>
<td>0.13</td>
</tr>
<tr>
<td>Maximum meaning</td>
<td>0.10</td>
<td>0.43</td>
<td>0.05</td>
<td>0.026</td>
<td>0.012</td>
<td>0.04</td>
<td>0.03</td>
<td>0.05</td>
<td>0.007</td>
<td>0.005</td>
<td>0.01</td>
<td>0.0008</td>
<td>0.008</td>
<td>0.01</td>
<td>0.007</td>
</tr>
<tr>
<td>Minimum meaning</td>
<td>0.07</td>
<td>0.32</td>
<td>0.02</td>
<td>0.015</td>
<td>0.006</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.005</td>
<td>0.005</td>
<td>0.01</td>
<td>0.0008</td>
<td>0.008</td>
<td>0.00</td>
<td>0.005</td>
</tr>
<tr>
<td>Difference</td>
<td>0.03</td>
<td>0.11</td>
<td>0.03</td>
<td>0.011</td>
<td>0.006</td>
<td>0.02</td>
<td>0.01</td>
<td>0.03</td>
<td>0.002</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.01</td>
<td>0.002</td>
</tr>
</tbody>
</table>
Fig. 1. Multifunctional modifiers [14]

From a comparison of the data in Table 2, it follows that because of the modification of St1kp, the average content of elements has changed as follows:

- the average carbon content increased by 0.004%, which reduces the breakage of hot-rolled wire;
- the silicon content has decreased to 0.03% instead of 0.05%, thereby reducing the likelihood of the formation of steel-embrittling silicon monoxide SiO;
- the concentration of harmful impurities has significantly decreased: sulphur by 1.2 times, phosphorus by 2 times;
- the amount of harmful gas impurities, including nitrogen, decreased by 1.167 times.

Modified steel St1kp contains 0.005% residual aluminium, while no residual aluminium was detected in serial unmodified steel. This indicates insufficient assimilation of aluminium ingot by the melt of serial steel and, consequently, under deoxidation of the steel.

That is, the modification made it possible to normalize the content of useful components of steel (C, Si, Al) and significantly reduce the number of harmful impurities (S, P, N). For converter steel, it was very important to reduce the amount of phosphorus by more than 2 times, since the process in these melting units does not involve dephosphorization due to the need to reduce significantly its productivity. Previously, for other steel grades treated with special deoxidizers–modifiers, their dephosphorization effect was found [16]. However, such a significant degree of dephosphorization (by 87%) was obtained for the first time.

### 3.2. Structure of the Reinforcing Steel St1kp

St1kp steel is used for reinforced concrete structures, for example, for residential buildings, pedestrian and automobile bridges. If you use ordinary serial steel, you can get a process that is shown in Fig. 2, a. The load, not meeting the resistance of grain boundaries, will destroy the material faster, and such steel will simply not be able to serve the pe-
Influence of Modification on the Characteristics of Reinforcing Steels

Fig. 2. Steel structure St1kp: serial (a) and modified (b) [13–15, 21]. Scale: ×600

period that is planned according to standards or specifications. After the modification, the grain structure of the St1kp steel was refined (Fig. 2, b), after which, it can be safely asserted that such a material can last longer. As shown in Fig. 2, b, the load will simply attenuate, encountering grain boundaries on its way, because of which such a material may even last longer than the time specified in the specifications or standards. The reason for this is the fact that, during modification, crystallization centres are formed because of interaction with the steel melt of special multicomponent modifier deoxidizers. They are quite evenly distributed in the volume of the metal due to the special physical and chemical properties, the composition of modifier deoxidizers, the constancy of their geometric shape and mass. As a result, the microstructure of the modified steel differs from the serial unmodified steel in greater uniformity of grains and less uneven grain size. Processing of the results of measuring grain sizes by the secant method [17] of modified and unmodified steels was carried out using the Alloys1 program written in C++ in the Borland Builder 5 environment. The average grain sizes in samples of modified steel turned out to be 1.91 times smaller than in unmodified steel: 22 µm in serial unmodified steel St1kp and 11.5 µm in modified steel of the same grade (Fig. 3).

The phase composition of steel St1kp was also studied using the method of x-ray diffraction analysis. The presence of α-ferrite and Fe₃C in the structure of St1kp steel was established, and the maximum intensity of x-ray interference lines of

Fig. 3. Reducing the grain size of mild steel St1kp under the influence of inoculation [13–15, 21]
\[ a = 2.8679 \text{ A}, \quad L_1 = 1428, \quad L_2 = 1572, \quad L = 2110 \text{ A}, \quad M = 4.72 \cdot 10^{-4}, \quad D = 3.89 \cdot 10^{10} \text{ cm}^{-2} \text{ dnu} 201. \]

\[ a = 2.8687 \text{ A}, \quad L_1 = 1321, \quad L_2 = 1500, \quad L = 2110 \text{ A}, \quad M = 4.76 \cdot 10^{-4}, \quad D = 4.5 \cdot 10^{10} \text{ cm}^{-2} \text{ dnu} 201. \]

\[ \alpha \text{-ferrite in the modified metal turned out to be lower than in the unmodified metal (Fig. 4).} \]

From the presented data, it is also seen that the amount of cementite in the modified steel is greater than in the serial unmodified steel, which follows from the ratio of the intensity of the Fe\(_3\)C peaks of the modified and unmodified serial St1kp steel.

In order to establish the effect of modification on the parameters of the fine structure, the periods of crystal lattices, the sizes of the regions of coherent scattering, microdistortions of the crystal lattice, and the density of dislocations were determined (Table 3).

Analysis of the data presented in Table 3 allows us to draw the conclusions below.

(i) The lattice period of the ferrite of the modified steel is decreased by 0.358% compared to the unmodified steel. This indicates an increase in the interatomic bonding forces in the crystal lattice of the modified steel ferrite. The sizes of blocks in the \(\alpha\)-phase along the (110) and (220) crystal directions after modification are decreased by 7.5% and 4.6%, respectively.

**Table 3. Fine structure parameters of modified and serial unmodified steel St1kp [13, 15, 21]**

<table>
<thead>
<tr>
<th>Steel type</th>
<th>Crystal lattice period of (\alpha)-ferrite, nm</th>
<th>Block sizes, nm</th>
<th>Microcrystal lattice distortion, (M)</th>
<th>Density dislocation, (D), cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>serial modified</td>
<td>0.28790</td>
<td>14280</td>
<td>15720</td>
<td>21100</td>
</tr>
<tr>
<td></td>
<td>0.28687</td>
<td>13210</td>
<td>15000</td>
<td>21100</td>
</tr>
</tbody>
</table>

[Fig. 4. X-ray diffraction pattern of samples of serial (a) and modified (b) steel grade St1kp](image-url)
(ii) The value of microdistortions is increased by 0.85% due to modification.
(iii) The dislocation density $D$ is noticeably increased under the influence of modification (by 18%) due to changes in block sizes and microdistortions.

3.3. Mechanical Characteristics of the Reinforcing Steel St1kp

The results of statistical processing of the mechanical characteristics of the finished steel grade St1kp serial and modified heats are given in Table 4. As seen, the mechanical properties of low-carbon modified steel of this grade are distinguished by high parameters of both stability and level in general.

All parameters of the mechanical properties of the modified metal met the requirements of DSTU 2770-94. This is especially important for reinforced concrete structures since the insufficient level of mechanical properties and their instability cannot guarantee the reliability and durability of their operation. During the solidification of the modified ingot, there is mainly volumetric crystallization, rather than heat-sink-oriented crystallization, as for serial metal. The predominant mechanism of volumetric crystallization is one of the main reasons for the stabilization of the chemical composition and the increase in the level of mechanical properties of steels under the combined effect of alloying components and harmful impurities of steel, both serial and melts modified with multifunctional modifiers (Fig. 5).

It is also possible to improve the properties of reinforcing steels by rolling. Its technological process of profiles of a simple geometric shape (reinforcement, wire rod) with longitudinal separation was implemented

<table>
<thead>
<tr>
<th>Statistical parameters</th>
<th>Mechanical characteristics (final)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_u$, MPA</td>
</tr>
<tr>
<td><strong>Serial</strong></td>
<td></td>
</tr>
<tr>
<td>max</td>
<td>395</td>
</tr>
<tr>
<td>min</td>
<td>360</td>
</tr>
<tr>
<td>Average value</td>
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</tr>
<tr>
<td>Parameter content difference</td>
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</tr>
<tr>
<td><strong>Modified</strong></td>
<td></td>
</tr>
<tr>
<td>max</td>
<td>395</td>
</tr>
<tr>
<td>min</td>
<td>370</td>
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<tr>
<td>Average value</td>
<td>380.8</td>
</tr>
<tr>
<td>Parameter content difference</td>
<td>25</td>
</tr>
</tbody>
</table>
in the 1980th of the last century and exported with a continuous small-section mill 320/150 built in 1985 [18]. This mill was equipped with a temper-type reinforcing steel thermomechanical hardening unit, which provides for separate cooling of each of the paired rolls in autonomous lines with individual water supplies.

The original rolling process developed and implemented later with the separation of reinforcing sections at the already operating mills of OJSC ‘ArcelorMittal Kryvyi Rih’, equipped with installations for hardening rolled products produced using conventional technology, required the search for new methods for forced cooling of paired rolls. To apply the well-known technology of forced cooling of paired rolls separately in autonomous lines with individual water supplies, it was necessary to almost double the high-pressure water consumption at existing plants, which was impossible to implement in the conditions of OJSC ‘ArcelorMittal Kryvyi Rih’ without a major reconstruction of the water supply systems of the rolling mill.

Considering the above, for the thermomechanical hardening of paired bars of reinforcing steel, a method was developed that included separate cooling of the bars at the exit from the rolling stand, followed by joint cooling of the paired bars in one coolant flow and further cutting of the paired bars into cooler lengths [19].

The implementation of this method of cooling paired rolls in the conditions of OJSC ‘ArcelorMittal Kryvyi Rih’ made it possible to organize the production of thermomechanical hardened reinforcing steel of classes A400C and A500C instead of hot-rolled steel during splitting rolling without reconstructing the existing water supply systems of rolling shops. The practical consumption of high-pressure water increased by only 15–20% compared to single rolling.

The specified method of cooling paired rolls (1) is carried out in the developed device (Fig. 6), which includes two independent cooling lines with injection nozzles (2) and water supply to each separate cooling chamber (3) and a common chamber (4) for joint cooling of paired rolls.
Influence of Modification on the Characteristics of Reinforcing Steels

...equipped with a wastewater cutter (5). The operation of the cooling device is carried out as follows.

Paired rolls of reinforcing profiles (1), leaving the last stand of the mill (Fig. 6), enter separately into autonomous cooling lines and having passed through the separate cooling chambers (3), converging at an angle to the centre line of the mill, together with the water flow, they enter the joint cooling chamber (4), where the temperature of the rolls is reduced to the required one. At the exit from the joint cooling chamber (4) of the paired rolls, the device (5) cuts off the wastewater and the rods exit the thermal hardening unit and are then cut by flying shears (6) into the lengths of the cooler.

A high set of characteristics of thermomechanical hardened steel reinforcement with the selected technology of interrupted hardening is ensured by the creation of a layered (composite) structure over the section of the rolled product, and the integral aggregate properties of a rod with such a structure are determined by the properties and volume fraction of each layer.

...Heat processing is also used, which also allows to increase the level of mechanical characteristics by 5–7%. Additional information about the formation of the structure of the martensitic layer adjacent directly to the surface was practically not revealed by the present studies. Appearing as a continuous layer over the entire surface with such a cooling duration that provided the reinforcement with approximately $\sigma_s = 510$ MPa, the martensite layer subsequently monotonously increased [20].

In this case, the formation of a martensite layer near the surface of the reinforcing bar occurs since the cooling rate here is supercritical. However, under stable conditions of thermal hardening, with distance from the surface, the cooling rate gradually decreases. When it becomes less critical, before the martensitic transformation occurs, some of the austenite will experience an intermediate transformation. In accordance
with the TKD (Fig. 7) for steel grade St3, this will happen at speeds less than 370 °C/s. As the calculations confirm, during thermal hardening in the flow of rod reinforcement with a diameter of 12 mm, the cooling rates become less than the specified value when moving away from the surface by more than ≈2.0 mm. Therefore, starting from these distances, the structure of the rods, which is formed directly during the period of intense cooling, will no longer be martensitic, but bainitic–martensitic, although with a predominance of the latter component.

Thus, the volume adjacent to the surface, in which the structure is formed directly during the cooling period, is the volume, the transformations in which are fully described by data generalized in the form of TCD, studies of the formation of the steel structure during continuous cooling. As expected, at all points of the ‘central’ volume, the structure is formed according to a single kinetics at the stage of final slow cooling in air after the completion of intensive cooling and equalization of temperature over the rod cross-section. However, the obtained research results showed that the kinetics of phase transformations is not uniform throughout the ‘central’ volume. As established, in the composition of the volume of the reinforcing bar, in which the structure is formed after the termination of intensive cooling, one should distinguish between the circumvaginal volume, which is from the axis of the rod to the surface by 0.67–0.70 of the radius length, and the volume between the circumvaginal volume and the layer martensite formed during the period of intense cooling.

In the near-axial volume during the decomposition of austenite, in fact, cooling conditions take place, containing elements of both continuous cooling and isothermal decomposition. In this case, the structure, as
the degree of hardening increases, successively changes from ferrite–pearlite (Fig. 8, a) to ferrite–pearlite–bainite (Fig. 8, b), ferrite–bainite–martensite (Fig. 5, c), and bainite–martensite (Fig. 8, d).

To ensure the required structure and the required level of mechanical properties of serial wire rod, after the end of deformation, it is subjected to ‘sprinkling’ according to the idea of Acad. K.F. Starodubov and development of it. If the first plant operated with spraying water jets in one mode, then in recent years, after the Zot Nekrasov Ferrous Metallurgy Institute of the National Academy of Sciences of Ukraine development and PC ‘ArcelorMittal Kryvyi Rih’, the heat processing of wire rod from rolling heating has been improved, made it more flexible. At present, it is possible to control the process of heat treatment from rolling heating with the help of computer automation, changing the rate of water pouring during a sprinkling, that is, intensifying the cooling rate of the wire rod, as well as the speed of its movement. Depending on the cooling rate, according to the data OJSC ‘ArcelorMittal Kryvyi Rih’, it became possible to obtain structures $F + P$ (ferrite + pearlite), $F + P + B$ (ferrite + pearlite + upper bainite), $F + P + B + C$ (ferrite + pearlite + upper bainite + structure-free cementite). Depending on the type of structure, the strength of the wire rod changes.

This technology allowed increasing the strength by 5%. However, the metal, having a number of disadvantages for a special purpose, needed improvement. One of the possible ways, in addition to modifica-
tion, was the development of optimal heat treatment from rolling heating. For its development, thermokinetic diagrams of the state of St1kp steel of modified and serial melts were built.

Depending on the carbon content in the steel, the cooling mode changed. For the modified steel, a thermokinetic state diagram has been constructed, which allows, depending on the requirements, to control all the technical temperature–time parameters of the processing process (Fig. 7). Depending on the production of sorbitol, pearlite, troostite, martensite, the process parameters are regulated in the structure according to the data of the thermokinetic diagram. All kinds of structures in the processing of St1kp metal with rolling heating according to the K.F. Starodubov’s idea and development obtained by us for the modified steel St1kp (Fig. 9).

Fig. 7. Thermokinetic diagram of austenite decomposition of modified (dark line) and serial (light line) steel St1kp [21]

Fig. 10. Microstructure of the modified St1kp steel samples (×500) at different cooling rates \( V_c \) and tempering temperatures \( T \) [21]: (a) \( V_c = 3.6 \, ^\circ\text{C}/\text{s} \) and \( T = 795 \, ^\circ\text{C} \); (b) \( V_c = 3.6 \, ^\circ\text{C}/\text{s} \) and \( T = 700 \, ^\circ\text{C} \); (c) \( V_c = 3.6 \, ^\circ\text{C}/\text{s} \) and \( T = 670 \, ^\circ\text{C} \); (d) \( V_c = 3.6 \, ^\circ\text{C}/\text{s} \) and \( T = 570 \, ^\circ\text{C} \)
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In hot-rolled metal after deformation and heat treatment by sprinkling wire from rolling heating, studies were carried out on the distribution of elements in the metal using a microscope JEOL Superprobe 733 (Japan).

Fig. 11. Non-metallic inclusions in standard St1kp steel at various magnifications [13–15, 21]: (a) \( \times 1400 \), (b) \( \times 8500 \), (c) \( \times 600 \)

<table>
<thead>
<tr>
<th>Point number</th>
<th>O</th>
<th>S</th>
<th>Fe</th>
<th>Total,%</th>
</tr>
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<tbody>
<tr>
<td>025</td>
<td>12.77</td>
<td>0.33</td>
<td>86.9</td>
<td>100</td>
</tr>
<tr>
<td>026</td>
<td>16.58</td>
<td>0.52</td>
<td>82.9</td>
<td>100</td>
</tr>
</tbody>
</table>

Fig. 12. Non-metallic inclusions in St1kp steel treated with a multifunctional modifier deoxidizer: (a) globular non-metallic inclusion (\( \times 1200 \)), (b) a single globular inclusion without corrosion locations, (\( \times 9000 \)) [13–15, 21]

<table>
<thead>
<tr>
<th>Point number</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>S</th>
<th>Mn</th>
<th>Fe</th>
<th>Total,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>032</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>75.32</td>
<td>100</td>
</tr>
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</table>

In hot-rolled metal after deformation and heat treatment by sprinkling wire from rolling heating, studies were carried out on the distribution of elements in the metal using a microscope JEOL Superprobe 733 (Japan).
On the installation for constructing thermokinetic diagrams of the decomposition of austenite, a diagram was constructed for modified and unmodified steel. Due to the wide time interval for cooling samples from $10^{-1}$ to $10^4$ s, the abscissa scale is given in the logarithmic version. The setup included an oven for heating the samples, a PDT 4 potentiometer, a recorder, and a computer with which the structures were displayed on a microscope for photographing. The cooling media were air, water, salted (10% NaCl) water. To construct a thermokinetic diagram of the decomposition of austenite in modified samples, they were heated to the critical point and cooled at different rates. Then, they were pressed in order of increasing cooling rates; thin sections were made and photographed. Then, hardness was measured on sections and plotted on cooling curves (Fig. 10). Based on the analysis of thermokinetic diagrams of state, microstructure of hardness, the temperature–time mode of cooling of wire rod from modified steel was determined: the cooling rate should be in the range from 1.6 to 3.6 deg/s, and the heat-treatment temperature from rolling heating $<670$ °C.

Consequently, the austenite in it is more stable due to the greater degree of alloying, which is justified by the greater stability of the chemical composition. Recommended microstructure (P + P) for modified steel corresponds to Fig. 10, c and d. They differ in that the diagram for unmodified steel is shifted to the left and down with respect to the decay diagram for the modified metal.

3.4. Non-Metallic Inclusions in the Reinforcing Steels

The above statements confirm the study of samples of hot-rolled St1kp bars of mass production and modified melts for non-metallic inclusions. An analysis of serial 34 industrial melts of St1kp steel showed that such a metal is more susceptible to corrosion [22], especially under conditions of long-term use, since in places with different concentrations of elements, enhanced corrosion is possible with the destruction of the integrity of the material. Figure 11 shows the centres of local corrosion destruction of the metal that have arisen on the surface of a serial wire rod.

The yellowish colour indicates the presence of corrosion products in the form of iron oxides. Their existence we confirmed experimentally using a JEOL JSN 636 LA scanning electron microscope equipped with a JED 2300 system. As can be seen from the figures, corrosion products with a high iron concentration are located in the corrosion damage zone (Fig. 11, a).

The reasons for such an extensive damage to the metal of serial melts of steel grade St1kp could be as follows:

- different alloying in adjacent wire rod microsections;
- uneven grain size in metal microvolumes;
- the presence of microstresses in the wire rod metal;
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- the variety of different types of microdefects [23–31] on the surface of the wire rod, namely, sulphide in the sample at hand.

The modifier–deoxidizer [14] globularizes non-metallic inclusions and neutralizes corrosion centres (Fig. 12), thereby creating additional crystallization centres, while the strength of the metal increases.

For the modified metal, we established as follow:
- the number of non-metallic inclusions is 2 times less than in serial steel, due to the treatment of the melt with multicomponent deoxidizers–modifiers;
- the size of non-metallic inclusions is much smaller from 2 to 7 microns due to their globularization; having a lower density in the composition of the complex compound of the elements Mg, Al, Si, S, they easily float into the slags or waste products [32, 33];
- there no corrosion centres were found in the modified metal, since it is microalloyed with such components as Ti, Mn, Cr, Cu, and V.

4. Conclusion

In conclusion, it should be noted that the work proved the effectiveness of the use of multifunctional modifiers, since they not only reduce the concentration of impurities such as sulphur, phosphorus, nitrogen, but also contribute to the stabilization of the chemical composition and mechanical characteristics of steel St1kp with their simultaneous increase. At the same time, under the influence of the components in the modification process, the structure of the studied metal improves with a simultaneous improvement in the morphology of non-metallic inclusions, which as a result improves the quality of the finished reinforcement, as well as increases its service life.

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ВПЛИВ МОДИФІКУВАННЯ НА ХАРАКТЕРИСТИКИ АРМАТУРНИХ КРИЦЬ, ПРИЗНАЧЕНИХ ДЛЯ ЗАЛІЗОБЕТОННИХ КОНСТРУКЦІЙ

Оглянуто й проаналізовано причини дестабілізації хемічного складу та механічних характеристик арматурних низьковуглецевих криць, а також представлено способи вирішення таких проблем. Визначено, що нестабільність хемічного складу та неметалеві включення включена витягнутої та гострокутної форми, що містять надмірну кількість газових та інших домішок, понижують термін експлуатації готового металургійного виробу та призводять до погіршення якості готової продукції. Встановлено та доведено, що одним із способів, що уможливлюють найбільш максимально стабілізувати хімічний склад і поліпшити механічні характеристики, а також якість арматури, є оброблення розтопів криць модифікаторами багатофункціональної дії. Визначено, що криця Ст1кп, як і інші низьколеговані криці, є багатокомпонентною системою, що складається з 17 і більше компонентів. Кожна з домішок, а також елементи-розкиснювачі-модифікатори (Al, Ti, Mg) можуть помітно змінювати склад неметалевих включень, основної матриці, цементиту, розмір зерна, механічні властивості та їхню стабільність. Встановлено, що після модифікування відбулось подрібнення зерен зернистої структури криці Ст1кп майже вдвічі, після чого можна сміливо стверджувати, що такий матеріал зможе прослужити довше. Виявлено, що всі параметри механічних властивостей модифікованого металу відповідали вимогам ДСТУ 2770-94 та перевершували також серійні. Це особливо важливо для залізобетонних конструкцій, оскільки недостатній рівень механічних властивостей та їхня нестабільність не можуть гарантувати надійність і довговічність їхньої експлуатації. Зазначено, що під час тверднення модифікованого зливка має місце в основному об’ємна, а не орієнтована тепловідведення кристалізація, як для серійного металу. Переважний механізм об’ємної кристалізації є одною з основних причин стабілізації хемічного складу та підвищення рівня механічних властивостей криць під комплексним впливом легувальних компонентів і шкідливих домішок криці, як серійних, так і модифікованих багатофункціональними модифікаторами розтопів. У роботі доведено, що після модифікування значно поліпшується морфологія неметалевих включень. У результаті якість готової арматури значно підвищується. Ключові слова: арматура, криця Ст1кп, модифікатори багатофункціональної дії, хемічний і фазовий склади, структура, густина дислокацій, механічні характеристики, неметалеві включення.