OPTIMIZATION OF PRODUCTION PROCESS OF STRUCTURAL STEEL MODIFIED WITH NITROGEN AND VANADIUM

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Abstract. Structural steels are the most promising material, particularly in machine design. An important issue is to match their properties with the exploitation demands. It can be achieved by the optimization of the steel production process, i.e. formation of the primary and secondary structure under modification with nitrogen and vanadium, proposed in this research. At the experiments the structural steels were melted, modified with nitrogen and vanadium, subsequently deoxidized with aluminium, cerium, and lanthanum. The steel samples were tested to reveal the mechanical properties and study the effect of modifying processing. The results have shown that some decrease in plastic properties, the impact strength and an increase in the critical temperature of brittleness is not due to vanadium nitride hardening of steel, but could be associated with imperfect technology. The final deoxidation of steel is often performed with aluminum of at least 0.05% in order to stabilize the grain of the structure during austenitizing heating. It was established that the necessary condition for the effective influence of nitrogen and vanadium should be a higher formation temperature of vanadium nitrides than aluminum nitrides in steels. Calculations showed that this condition is realized when the content of aluminum in steel is less than 0.03% and vanadium - 0.10%. The results of the performed experiments have shown that in this case there is a simultaneous increase in the strength properties and impact toughness of steel. Based on the obtained results the recommendations for the industrial process of steel making was formulated as below. In foundry shops with inductional melting furnaces it is necessary to additionally deoxidize steel with cerium and lanthanum. So, comprehensive optimization of the content of nitrogen, vanadium and deoxidizers in steel, as well as the temperature of austenitizing heating ensure increase in mechanical properties without reduction in plasticity and toughness.

Keywords: structural steels, modifying, deoxidation, aluminium, cerium, nitrogen, vanadium.

Introduction

Structural steels are the most used material in mechanical engineering. An important task is to ensure that the level of their mechanical properties corresponds to the loads and operating conditions. One of the most effective ways to improve these properties is to influence the process of formation of the primary and secondary structure of structural steels through modification with nitrogen and vanadium [1-5]. Many researchers have found that decrease in the plastic properties, impact strength and increase in the critical temperature of brittleness observed during such processing is not a natural consequence of vanadium nitride hardening of steel, but is associated with the imperfection of the technology. By comprehensive optimization of the content of nitrogen, vanadium and other nitride-forming elements in steel, as well as the temperature of austenitizing heating, such undesirable effects could be avoided.

The thermodynamic models of carbonitride precipitation in high strength low alloyed steels containing up to three microalloying elements with or without additions of aluminum, the composition of V(C,N) as precipitated file in HSLA steels microalloyed with vanadium, modeling of the kinetics of carbonitride precipitation process in high-strength low-alloy steels using cellular automata method and modeling of the kinetics of the carbonitride precipitation process in microalloyed steels are shown in works [6-9]. Therefore, it was possible to calculate the effect of temperature on the chemical composition of VCₓN₁₋ₓ carbonitride, the content of undissolved compounds, metallic elements dissolved in austenite and the amount of dissolved nitrogen.

The final deoxidation of steel is almost always provided by aluminum, and its content in steel is recommended to be more than 0.05% in order to stabilize the structure during austenitizing heating. However, it is known that the free energy of formation of aluminum nitrides is of 80 J·kg⁻¹ x atom less than that of vanadium nitrides [10]. Therefore, the necessary condition for the effective influence of nitrogen and vanadium on the structure and properties of aluminum deoxidized steel should be a higher temperature of vanadium nitrides (tVN) formation then of aluminum nitrides (tAlN).

DOI: 10.22616/ERDev.2022.21.TF085
However, a stable content of residual aluminum in steel in the range of 0.01–0.02% (wt. fraction) is easily achieved only when pouring large masses of metal. Under the conditions of small-portion shaped casting, the degree of assimilation of aluminum during smelting and its secondary oxidation during casting are less stable. This is the possible reason of uneven deoxidation in foundry when small induction melting furnaces are used. So, it is necessary to additionally deoxidize the steel with elements of high affinity to oxygen and a higher free energy of nitride formation.

The literature analysis shown that rear earth metals (REM) are suitable to be used because they first initiate steel deoxidation and then formation of oxisulfides, sulfides and, finally, nitrides [11]. In steels with nitride vanadium strengthening deoxidation with Al, Ti and Zr before REM additions is not effective because they form more stable nitrides then vanadium.

The research on lanthanum, cerium, vanadium and aluminum nitrides release in γ-iron show that lanthanum and cerium nitrides are doing so when the concentrations of cerium and nitrogen in the solid solution exceeds 1.7-3.7 times that of vanadium and 7.8-18.4 times compared to aluminum [12].

The aim of the article is to optimize the content of nitrogen, vanadium and deoxidizers in steel, as well as the temperature of austenitizing heating, which would provide an increase in the strength properties without reducing in ductility and toughness.

Materials and methods

The smelting of the original steels was carried out in induction furnace of 160 kg with a basic lining. In total six laboratory heats of steel were done. The chemical composition of steels was varied by alloying and include as follow (wt.%): 0.19-0.50 C; 0.2-0.72 Si; 0.53-0.98 Mn; 0.005-0.018 N; up to 0.12 V. Carbon was added in charge, whereas other elements (Si, Mn, N and V) were introduced into the melt as ferroalloys at 1600 °C. The content of S in the melts was in the range of 0.018-0.020 wt.%, P = 0.005-0.007 wt. %.

After melting the charge, the melt was deoxidized with Mn and Si and then poured into a 30 kg ladle. When pouring into the first ladle, the metal was deoxidized with 0.1% Al (residual content of Alres = 0.06% wt. fraction) and 0.15% SiCa, and when pouring into the second ladle – 0.04% Al (0.02% Alres), 0.15% SiCa, 0.01% V. The rear earth metals of 0.25% were introduced into the metal remaining in the furnace. The residual content of REM depending on the holding time is as follows: after 2 min – 0.12%; 4 min – 0.08%; 6 min – 0.05%; 10 min – 0.04%; 12 min – 0.02%. To display the maximum refining effect of REM and obtain a stable residual content of cerium (Ce < 0.06%), the melt was kept at 1600 °C for 8 min. Then part of the metal was poured into the third ladle, in which it was deoxidized with 0.15% SiCa. After that ferrovanadium ligature ZhVdN (TU 14-139-75) was introduced into the remaining steel in the furnace bath to get of 0.1% V and 0.01% N in the melt. So, the differentiated N content (within 0.005-0.018%) was achieved by partial steel pouring out and ligature processing.

When pouring into the fourth ladle, the metal was also deoxidized with 0.15% SiCa, the residual content of Ce is of 0.04%. The detailed data of every steel heats, the chemical composition and processing parameters, i.e. temperature and holding time are shown in Table 1.

The content of gases in steels was determined by the vacuum melting method [13]. The chemical composition of the steels was determined using a SPAS-05 optical emission spectrometer. After melting steel was cast into the ceramic molds at 1550 °C. Thus, the standard samples with a diameter of 100-140 mm and length of 220-340 mm were obtained for thermal treatment and mechanical testing.

The test bars were made in accordance with the requirements of [14]. The standard samples of the length $L = 83$ mm, $l_0 = 50$ mm and diameters $D = 11$ mm, $d_0 = 5$ mm were cut to determine the mechanical properties [15]. At the normal temperature the UTS-100 installation was used to measure the strength and tensile limit, the relative elongation and narrowing at strain in accordance with the recommendations of [15], and the impact toughness, accordingly [16]. When determining the mechanical properties, one measurement point corresponded to the arithmetic mean of the test results of 3 samples.

The pair correlation analyses were carried out according to the methodology in [17].
Results and discussion

To effectively control the process of formation and dissolution of the secondary phases, i.e. vanadium, aluminum, and cerium nitrides in austenite, using the method given in [18], the temperature dependences of the interaction parameters and the concentration dependences of the influence of alloying elements on the change in the equilibrium temperature of these phases in austenite were determined.

Effect of deoxidation modes on the mechanical properties of carbon structural steels modified by nitrogen and vanadium after normalization

<table>
<thead>
<tr>
<th>No</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>V</th>
<th>N</th>
<th>Al</th>
<th>Ce</th>
<th>Temperature, °C; (Holding, hour)</th>
<th>Tensile strength, MPa</th>
<th>Yield point</th>
<th>Elongation</th>
<th>Reduction of area</th>
<th>Toughness 20 °C (-60 °C), MJ·m⁻²</th>
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</thead>
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<tr>
<td>1/1</td>
<td>0.29</td>
<td>0.20</td>
<td>0.61</td>
<td>-</td>
<td>0.005</td>
<td>0.048</td>
<td>-</td>
<td>920 (4) 1150 (4)</td>
<td>539 524</td>
<td>325 319</td>
<td>22 24</td>
<td>35 45</td>
<td>0.66(0.16) 0.67(0.17)</td>
</tr>
<tr>
<td>1/2</td>
<td>0.29</td>
<td>0.20</td>
<td>0.61</td>
<td>-</td>
<td>0.06</td>
<td>0.010</td>
<td>0.044</td>
<td>-</td>
<td>554 552</td>
<td>341 363</td>
<td>21 23</td>
<td>40 30</td>
<td>0.63(0.27) 0.70(0.28)</td>
</tr>
<tr>
<td>2/1</td>
<td>0.32</td>
<td>0.24</td>
<td>0.71</td>
<td>0.05</td>
<td>0.010</td>
<td>0.030</td>
<td>-</td>
<td>980 (4)</td>
<td>583 323</td>
<td>26 45</td>
<td>45</td>
<td>0.62(0.36)</td>
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</tr>
<tr>
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<td>0.09</td>
<td>0.014</td>
<td>0.020</td>
<td>-</td>
<td>980 (4)</td>
<td>637 392</td>
<td>18 24</td>
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<tr>
<td>2/3</td>
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<td>0.04</td>
<td>0.009</td>
<td>0.018</td>
<td>-</td>
<td>920 (4)</td>
<td>613 319</td>
<td>27 36</td>
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<tr>
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<td>0.10</td>
<td>0.015</td>
<td>0.011</td>
<td>-</td>
<td>632 392</td>
<td>28 59</td>
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<td>0.08</td>
<td>0.012</td>
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<td>-</td>
<td>920 (2)</td>
<td>510 345</td>
<td>29 48</td>
<td>102</td>
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<tr>
<td>4/2</td>
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<td>0.08</td>
<td>0.012</td>
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<td>-</td>
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<td>0.71</td>
<td>0.05</td>
<td>0.010</td>
<td>0.030</td>
<td>-</td>
<td>920 (6)</td>
<td>515 355</td>
<td>28 46</td>
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<tr>
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<td>0.009</td>
<td>0.018</td>
<td>-</td>
<td>920 (2)</td>
<td>505 365</td>
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<td>0.011</td>
<td>-</td>
<td>920 (4)</td>
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<td>0.021</td>
<td>-</td>
<td>Quenching 920 °C</td>
<td>700 545</td>
<td>20 43</td>
<td>0.45</td>
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<td>Quenching 960 °C</td>
<td>745 575</td>
<td>20 43</td>
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<td></td>
<td></td>
<td>Quenching 1000 °C</td>
<td>800 620</td>
<td>18 48</td>
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<td></td>
<td></td>
<td>Quenching 1040 °C</td>
<td>790 610</td>
<td>12 41</td>
<td>0.48</td>
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<tr>
<td>6/1</td>
<td>0.50</td>
<td>0.38</td>
<td>0.80</td>
<td>0.06</td>
<td>0.006</td>
<td>0.06</td>
<td>-</td>
<td>860 (2)</td>
<td>875 430</td>
<td>19 47</td>
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<tr>
<td>6/2</td>
<td>0.50</td>
<td>0.38</td>
<td>0.80</td>
<td>0.10</td>
<td>0.017</td>
<td>0.02</td>
<td>-</td>
<td>860 (2)</td>
<td>895 535</td>
<td>20 46</td>
<td>0.54</td>
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<td>6/3</td>
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<td>0.38</td>
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<td>0.02</td>
<td>-</td>
<td>860 (2)</td>
<td>920 655</td>
<td>20 43</td>
<td>0.56</td>
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<td>0.80</td>
<td>0.10</td>
<td>0.018</td>
<td>0.04</td>
<td>-</td>
<td>860 (2)</td>
<td>905 650</td>
<td>18 48</td>
<td>0.58</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The resulting equations have the following form:
\[ T_{VN} = \frac{-9473 + 2436[V] + 8950[N] + 932[C] + 160[Mn] - 67[Si] + 419[Cr] + 1610[Al] - 535[Ni] + 411[Ce] + 2659[Mo]}{\lg[V] + \lg[N] - 3.97 + 1.5[V] + 5.44[N] + 0.059[Si] + 0.128[Cr] + 0.0598[Mn] + 0.831[Al] + 0.196[Ce] + 0.408[C] - 0.0344[Ni] + 1.45[Mo]} \], \hspace{1cm} (1) \\


\[ T_{CeN} = \frac{-9040 + 700[C] - 271[Si] - 80[Mn] + 312[Cr] + 2461[V]}{\lg[Ce] + \lg[N] - 4.25 + 0.654[C] - 0.097[Si] + 0.106[Cr] + 1.5[V] + 0.067[Mn]} \], \hspace{1cm} (3)

where \([V], [N], [Mn], [Si], [Cr], [Al], [Ni], [Ce], [Mo]\) – the element content, wt.% in solid solution, respectively; \\
\(T_{VN}, T_{AlN}, T_{CeN}\) – equilibrium temperature in Kelvin of VN, AlN, CeN, accordingly.

The calculations by equations 1 and 2 show that conditions of the preferred vanadium nitride precipitation in steels presented in Table 1 during deoxidation with aluminum could be realized when the aluminum content in steel is less than 0.03% and vanadium exceeds 0.10% (Fig. 1, Table 2).

![Equilibrium temperatures](image)

**Equilibrium temperatures (°C) of nitride of V (**\(t_{VN}\)**), Al (**\(t_{AlN}\)**) and Ce (**\(t_{CeN}\)**) dissolution and precipitation in austenite of steels, numbers in parenthesis present steels from Table 1**

It should be also taken into account that according to the results in [11], from 0.01 to 0.02% of aluminum is going to form oxides.

**Table 2**

<table>
<thead>
<tr>
<th>Steel number</th>
<th>1/1</th>
<th>2/1</th>
<th>2/2</th>
<th>2/3</th>
<th>3/1</th>
<th>3/2</th>
<th>3/3</th>
<th>4</th>
<th>5</th>
<th>6/1</th>
<th>6/2</th>
<th>6/3</th>
<th>6/4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(t_{VN})</td>
<td>-</td>
<td>1016</td>
<td>1001</td>
<td>1076</td>
<td>1073</td>
<td>1076</td>
<td>1021</td>
<td>988</td>
<td>1104</td>
<td>1059</td>
<td>1119</td>
<td>1056</td>
<td>1056</td>
</tr>
<tr>
<td>(t_{AlN})</td>
<td>1079</td>
<td>1117</td>
<td>1079</td>
<td>1073</td>
<td>1021</td>
<td>1073</td>
<td>978</td>
<td>-</td>
<td>1056</td>
<td>1041</td>
<td>1125</td>
<td>1043</td>
<td>1043</td>
</tr>
<tr>
<td>(t_{CeN})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>930</td>
</tr>
</tbody>
</table>

*Calculations assume that 0.015% of Al goes to oxides*

The results of the experiments show that at a total weight fraction of Al = 0.044-0.048% (heat 1, fractions 1/1 and 1/2), alloying with nitrogen and vanadium, does not effectively increase the strength properties, although an increase in the impact strength is observed at minus 60 °C (Table 1). Calculations performed according to the model of H. Adrian [6] show (Fig. 2 a) that complete dissolution of the nitride phase in steel of heat 1 fraction 1/2 occurs at 1125 °C.
For dissolution of AlN and the secondary dispersed precipitation of the nitride phase, the temperature of the austenitizing heating was increased to 1150°C. In this case, a simultaneous increase in the strength properties and toughness is achieved.

With a decrease of total aluminum in steel to 0.02 - 0.03% (heat 2, fractions 2/1, 2/2, 2/3), a more significant increase in the strength properties of steel is achieved, especially when normalized from 980 °C, than that of 920°C. The high level of toughness is kept at room and negative temperatures. This is due to the fact that nitride precipitation changes from aluminum nitrides (heat 2, fractions 2/1, 2/2, Fig. 2b) to vanadium nitrides (heat 2, fraction 2/3, Fig. 2c).

A further reduction of aluminum to 0.011% with the addition of 0.1% V and 0.01% N provides the most rational increase in the mechanical properties including toughness at minus 60°C (heat 3). The subsequent changes in nitrides are observed in heat 3, fractions 3/2 (Fig. 2d) and 3/3 (Fig. 2e).

Fig. 2. Thermodynamic calculations of the content of undissolved V, Al, Ce compounds (a-g) and effect of temperature on the content of V, Al, Ce dissolved in austenite (h, i) [6]: (a-f) green lines – Al; (a-g) red lines – V; (g) green line – Ce; (h-i): solid lines – V; (h) dash line – Al; (i) dash line – Ce. Fraction chemical compositions according to Table 1: a – 1/2; b – 2/2; c – 2/3; d – 3/2; e – 3/3; f – 6/2; g – 6/4; h – 6/2; i – 6/4
Due to the fact that hardening of steel during normalization can be limited by both thermodynamic and kinetic parameters of dissolution of the nitride phase during austenitizing heating, we studied the effect of the temperature and the time factor of austenitization on the efficiency of changing the mechanical properties (Table 1, heat 4). As it can be seen from Table 1 (heat 4), an increase in the duration of heating at 920°C from 2 to 8 hours leads to a slight increase in only the yield strength. At 20 hours of heating, there is already a significant decrease in the strength properties and toughness of steel.

The study of the steel microstructure shows that 20-hour heating leads to coarsening the ferrite-pearlite structure (Fig. 3).

![Fig. 3. Effect of austenitizing heating of initial (a, b) and modified by nitrogen and vanadium (c, d) steels on the microstructure: a, c – duration heating at 920 °C – 4 hours; b, d – 20 hours; a, b – heat 3, fraction 3/1 of Table 1; c, d - heat 3, fraction 3/3 of Table 1. Magnification x 100](image)

Keeping in mind a decrease in the strength properties it is possible to conclude that at heating to 920°C the dissolution of the nitride phase is limited by the thermodynamic rather than the kinetic factors. Prolonged heating contributes to coagulation of undissolved vanadium nitrides when heated to 920 °C rather than an increase in the proportion of dissolved nitrides.

This explains the enlargement of the elements of the ferrite-pearlite structure, since the dispersed vanadium nitrides are the sites of the nucleation of ferrite centers.

With a reduced aluminum content, the temperature of austenitizing heating has a crucial influence on the effectiveness of vanadium carbonitride hardening. An increase in the heating temperature for quenching from 920 to 1000°C upon improvement (tempering at 600°C) leads to an additional increase in the strength characteristics by 85–100 MPa without reducing the ductility and toughness of the steel (Table 1, heat 5).

A further increase in the heating temperature is impractical, since it is accompanied by an intensive growth of austenite grains, enlargement of the elements of the ferrite-pearlite structure and the associated decrease in the characteristics of the mechanical properties.

However, when deoxidizing steel with a reduced amount of aluminum, an increase in the oxygen content in steel is observed (Table 3).

### Table 3

<table>
<thead>
<tr>
<th>No of table 1</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>V</th>
<th>Al</th>
<th>Ce</th>
<th>O</th>
<th>H, G per 100 cm³</th>
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<tr>
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<td>0.38</td>
<td>0.80</td>
<td>-</td>
<td>0.06</td>
<td>-</td>
<td>0.0058</td>
<td>0.006</td>
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<td>0.10</td>
<td>0.02</td>
<td>-</td>
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<td>-</td>
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<td>0.050</td>
<td>0.0025</td>
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<td>0.10</td>
<td>-</td>
<td>-</td>
<td>0.040</td>
<td>0.0043</td>
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</table>

The usage of REM reduces the amount of oxygen compared to deoxidation with 0.1% aluminum.

The analysis of the thermodynamic conditions for vanadium nitride precipitation in carbon steels with a low aluminum content (Table 1, heat 6, fraction 6/2) or deoxidized by REMs (Table 1, heat 6, fraction 6/4) showed preferred vanadium nitride phase precipitation (Fig. 2 f, g).

The study of the influence of the austenitizing heating temperature on the content of the vanadium nitride phase showed that, in the case of a low aluminum content in steel, about 19% of its total amount of vanadium in steel dissolves in austenite at a temperature of 860 °C, at 900 °C – 28%, 950 °C – 45%.
Accordingly, the amount of vanadium bound into nitrides at a temperature of 860 °C – 81%, 900 °C – 72%, 950 °C – 55%.

In the case of REM deoxidation about 20% of total vanadium content in steel is dissolved in austenite at a temperature of 860 °C, at 900 °C – 32%, 950 °C – 50%, 1000 °C – 73% (Fig. 2 i). Accordingly, the amount of vanadium bound into nitrides at a temperature of 860 °C is of 80%, 900 °C – 68%, 950 °C – 50%, 1000 °C – 27%.

The study of the effect of austenitizing heating temperature on the mechanical properties of carbon steels (Table 1, heat 6, fractions 6/1-6/4) showed that when steels are normalized in the case of a low residual aluminum content or final deoxidation of REM, an increase in the yield strength is achieved with 175-250 MPa, i.e. by 30-45%, by adding nitrogen and vanadium without reducing the plastic properties and toughness. At the same time, high absolute values of the strength characteristics and plastic properties are observed when steel is normalized from 950°C. Higher strength is achieved with normalization from 1000 °C. However, in this case, there is already a decrease in the plastic properties and toughness of the steel.

Thus, the final deoxidation with REM instead of aluminium at a proper austenitization temperature leads to an additional significant increase in the strength properties, ductility, and toughness of the steel. However, in the case of pouring steel from stop ladles, the use of REM is not always possible due to tightening of the ladle stop hole. Therefore, under such production conditions the most optimal steelmaking technology concerns ferrovanadium introduction into the melt in the furnace and alloying with nitrogen after the charge is melted, the impurities are oxidized, Mn and Si melt is deoxidized, and the steel is of the required chemical composition.

In the process of tapping the metal from the furnace 0.8-1.5 kg·t⁻¹ of SiCa is added to the jet, and aluminum deoxidizes in the ladle in the amount of 0.2-0.4 kg·t⁻¹. The final deoxidation with REM is more preferable than aluminum, because of the possibility of more reliable deoxidation of steel and a wider variation in the casting time. This is especially effective when pouring steel from a ladle through a spout, for example, in precision casting. In this case, after melting the charge and oxidizing impurities, 2-3 kg·t⁻¹ of rare earth metals are introduced into the melt in a furnace, held for 5-10 min, after which the melt is alloyed with nitrogen and vanadium, and in the process pouring steel into the ladle the melt is treated with SiCa in the amount of 1.0-1.5 kg·t⁻¹.

Optimization of deoxidation of steels containing nitrogen and vanadium is necessary but not sufficient for a comprehensive increase in the level of their physical and mechanical properties. The analysis of the results in Table 1 shows that another important factor influencing the properties of steel is the degree of deviation of the system from the equilibrium state, i.e. the equilibrium temperature of vanadium nitrides in austenite (Fig. 4).

![Fig. 4. Influence of Δt parameter on the yield point and toughness (KCU) of steel modified by nitrogen and vanadium: Δt- differences between the temperature of equilibrium vanadium nitrides in austenite (Equation 1) and austenitizing heating; chemical content of steel corresponds to 6/4 of Table 1](image)

It can be seen that in the case of the implementation of thermodynamic conditions for the preferential precipitation of vanadium nitrides ($T_{VN} = 1099$ °C, $T_{CeN} = 975$ °C) (Table 1, heat 6, fractions...
A significant increase in the level of steel properties is noted when heated by 150–200 °C below the temperature of complete dissolution of vanadium nitrides ($t_{VN}$). With a further increase in the heating temperature, the rate of increase in the yield strength decreases and a tendency to a decrease in the plastic characteristics is noted. Embrittlement of steel is observed at a heating temperature 150°C below the temperature of complete dissolution of vanadium nitrides (Fig. 3). Therefore, the optimum temperature, $t_a$, for austenitizing heating of steels with nitrogen and vanadium is determined by the following limits:

$$t_{VN} - 200 < t_a < t_{VN} - 150.$$  (4)

The analysis of the mechanical properties of Cr-Mn-Si steels modified with nitrogen and vanadium confirms the reliability of the conditions for optimizing the austenitizing heating temperature. For example, vanadium nitride hardening of steel 35KhGSL under optimal conditions of deoxidation and heating leads to an increase in the yield strength in the improved state by 115-140 MPa without reducing the level of the plastic properties.

**Conclusions**

The regularities of the influence of the chemical composition and structural state, associated with the modes of deoxidation by aluminum and cerium and heat treatment, on the mechanical properties and structurally sensitive service properties of structural steels are studied.

It has been established that a significant increase in the strength properties of steel while maintaining a high level of plasticity is achieved when the residual content of aluminum or cerium does not exceed 0.03 and 0.06 wt.%, respectively, the amount of insoluble vanadium nitride phase stabilizes the austenite grain, and a solid solution with nitrogen and vanadium is sufficient to increase its resistance to supercooling and effective dispersion strengthening of ferrite.

**Acknowledgements**

The authors are grateful to Professor H. Adrian of AGH University of Science and Technology, Poland for the valuable discussion while writing the article.

**Author contributions**

Y.A. conceptualization, methodology, experimentation, results analysing, writing – original draft preparation; S.G. formal analysis, experimentation, results discussion, writing – review and editing, H.M. experimentation, results discussion, draft preparation; V.K. thermodynamical calculations, writing – review and editing. All authors have read and agreed to the published version of the manuscript.

**References**


