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# Analysis of the reasons for the formation of defects in the 12-Cr18-Ni10-Ti steel billets and development of recommendations for its elimination

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ABSTRACT

**Introdution.** Austenitic steel (e.g., *AISI 304*, *AISI 321*, *AISI 316*, *AISI 403*, 12-Cr18-Ni10-Ti, etc.) is widespread, which is caused by high corrosion resistance and the corresponding possibility of use in aggressive media. The following most common types of 12-Cr18-Ni10-Ti steel defects can be distinguished: integranular corrosion, martensitic orientation of the $\alpha$-phase and ferrite $\delta$-phase. **The purpose of work:** to analyze the defects formation reasons of the 12-Cr18-Ni10-Ti steel grade billets and to develop recommendations for their elimination. **The methods of investigation.** Tests of 12-Cr18-Ni10-Ti steel samples for resistance to integranular corrosion, metallographic analysis of defects were carried out in this work. Hardness measurements were carried out for various degrees of billets reduction. Thermodynamic calculations of phase equilibrium in multicomponent steel for different temperatures were performed by the *Thermo-Calc* software. **Results and Discussion.** It is determined that in order to prevent integranular corrosion, it is necessary to reduce the nitrogen and carbon content in steel at the stage of ladle refining to 0.05%, and also to ensure the concentration of titanium in steel is not less than the permissible value — 0.3%. These measures contribute to the reduction of $Cr_{23}C_6$ chromium carbides responsible for integranular corrosion. It is necessary to reduce the degree of compression of the billets to a level of no more than 50% to prevent the appearance of a ferromagnetic martensitic α-phase, since the formation of this defect is associated with a high degree of compression during drawing. The high-temperature phase of δ-ferrite exists in the metal structure in a wide temperature range. Reducing this range to 100 degrees or less by optimizing the composition of the carbon and chromium alloy in accordance with GOST 5632-2014 leads to a significant reduction of the amount of ferrite. However, it is not possible to completely eliminate it from the structure of steel. For all cases, it is necessary to assign austenization of billets in the temperature range of 1,050…1,100 °C.

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## Introduction

Currently, *12-Cr18-Ni10-Ti* stainless steel has become quite widespread in power engineering because of its high corrosion properties, manifested in a significant range of application temperatures [1–5]. This is a reason why it is necessary to improve the quality of billets made of this steel, especially used in aggressive media. Therefore, all studies related to the most typical defects of *12-Cr18-Ni10-Ti* steel products and the search for recommendations aimed at its elimination are quite relevant.

It is known that the following main structural defects are most typical for *12-Cr18-Ni10-Ti* steel: intergranular corrosion, the presence of martensitic α-phase and ferrite $\delta$-phase [6–11].

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It is established that chromium carbides $Cr_{23}C_6$ are responsible for intergranular type of corrosion. Formation of these carbides along the boundaries of austenitic grains is responsible for the reduction of chromium dissolved in the matrix to values (less than 13%), providing a local drop in corrosion resistance [12–14]. This process is intensified during long soaking at temperatures corresponding to the active formation of chromium carbides, while corrosion spreads into the depth of the grain.

Some measures are implemented to reduce the tendency of *12-Cr18-Ni10-Ti* steel to this type of corrosion like heat treatment of billets (quenching, annealing), as well as optimization of the chemical composition forming during smelting and ladle treatment of liquid steel [15–17].

The formation of a martensitic *α*-phase in the structure of stainless steel may occur during working at low temperatures or in the process of cold deformation, accompanied by an increase in the magnetic properties of the material. This transition is undesirable for austenitic steel, so the chemical composition and rolling parameters are optimized in order to prevent it [7, 18].

The formation of ferrite *δ*-phase in this type of steel starts at the beginning of the solidification of the melt, then with further cooling the δ-ferrite phase dissolves in austenite. Due to the significant cooling rates of ingots, this process is usually incomplete. Even after hot plastic deformation, there is a residual ferrite phase in the metal structure, which degrades the magnetic properties. Moreover, the ductility and crack resistance of steel are reduced [19–20].

Today the methods of thermodynamic simulation are widely used to assess the influence of the chemical composition of materials on the number and type of phase constituents. Such information allows clarifying recommendations and measures to improve the quality of metal products [21–23].

*The purpose of work:*

– studying of the main defects typical for *12-Cr18-Ni10-Ti* stainless steel;

– performing thermodynamic simulation of the accompanying phase transformations;

– making recommendations for improving the quality of the metal and reducing its defects based on the studies and calculations.

## The methods of investigation

As part of this work, tests of *12-Cr18-Ni10-Ti* steel for resistance to intergranular corrosion were carried out in accordance with *GOST 6032-2017 “Corrosion-resistant steels and alloys”*. Oxide scale was removed from the surface of the heat-treated specimens by chemical etching, and then specimens were kept in a boiling aqueous solution of copper sulfate and sulfuric acid in the presence of metallic copper. Depending on the method, the holding time was 24 hours or 8 hours. After the tests, bending by 90 ± 5° and examination for cracks were carried out. The presence of cracks on the specimens bent after the test and the absence of cracks on the control specimens bent in the same way indicated the tendency of the steel to intergranular corrosion.

Preparation for metallographic analysis consisted of sequential grinding, polishing of stainless steel specimens and electrochemical etching in a 10% aqueous solution of oxalic acid. *Buehler Ltd* equipment was used for specimens preparation.

An additional austenization operation of the specimens could be carried out if necessary, namely, a long soaking in the range of 1,000–1,200 °C to remove magnetization and dissolve the ferrite phase. Metallographic analysis was carried out directly using a microvizor *Mkvizo-MET-221*.

Hardness measurements of the hard-worked metal specimens were carried out by a *TB 5015-01* tester using *Brinell* scale.

Thermodynamic simulation was performed using the *Thermo-Calc* software product. This program allows equilibrium calculations of multicomponent multiphase systems under different temperature conditions for various chemical compositions.

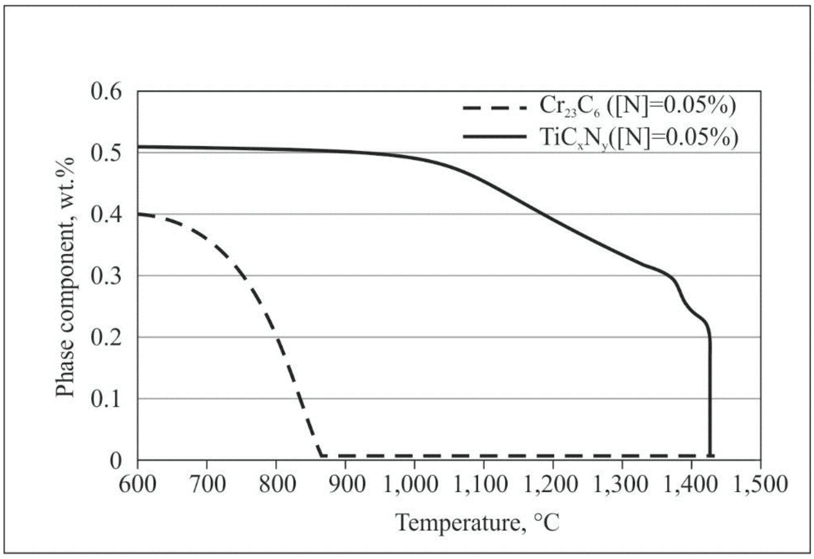
## Results and Discussion

### *The effect of the various components content on the formation of intergranular corrosion in stainless steel*

To identify the features of the intergranular corrosion development, stainless steel specimens were investigated according to the method described above. The presence of defects for various chemical compositions is noticed. Thermodynamic simulation was carried out for each composition — the quantity and the thermal nature of the forming carbide and nitride phases are estimated: titanium carbonitrides $TiC_xN_y$ and $Cr_{23}C_6$ carbides. The relationship between the increased amount of chromium carbides and the defects of stainless steel is found and confirmed.

Then temperature dependences of phase components in a wide range of various steel *12-Cr18-Ni10-Ti* components were calculated (for the initial composition taken: *C* = 0.08 %, *Cr* = 18 %, *Ni* = 10 %, *Mn* = 1.5 %, *Ti* = 0.4 %). The most significant elements are carbon and nitrogen.

Figure 1 shows the typical thermal nature of the carbide and nitride phases in the stainless steel for the range of nitrogen changes *N* = 0.05–0.10 %.

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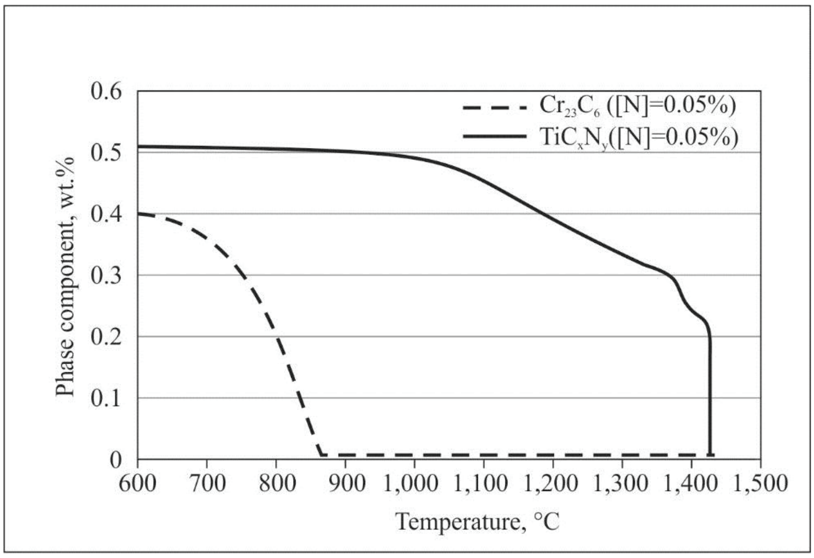


*b*

*Fig. 1.* Dependence of the content of chromium carbides $Cr_{23}C_6$ and titanium carbonitrides $TiC_xN_y$ on the nitrogen content in steel:

*a* – [N] = 0.05 %; *б* – [N] = 0.10 %

The process of titanium carbonitrides $TiC_xN_y$ formation begins at temperatures around 1,425 $^{o}$C. The higher the initial nitrogen content in the steel, the more titanium is consumed to form the nitride component of this phase, the less titanium binds carbon to carbide. Thus, conditions for the release of this carbon in the form of $Cr_{23}C_6$ carbides are created. With a significant nitrogen content (N = 0.1 %), chromium carbides are formed at 960 $^{o}$C and reach up to 1.15 wt.%, with a decrease in nitrogen to 0.05 %, the formation temperature drops by 100 $^{o}$C and the final mass is 0.41 wt.%.

Metallographic studies confirm that with an increase in the nitrogen content, there is an increase in the mass of chromium carbides $Cr_{23}C_6$, provoking intergranular corrosion. Without interacting with chromium, nitrogen indirectly increases the number of carbide phases by binding titanium.

The carbon content naturally and significantly affects the number of $Cr_{23}C_6$ compounds, so, with an increase in the carbon content, their mass and the temperature of the formation beginning grow up. The calculation results show that the critical value is C = 0.05 %, at which there is no release of chromium carbides, and a significant part of the carbon binds to titanium.

Thus, in order to minimize the formation of defects associated with intergranular corrosion, it is recommended to reduce nitrogen and carbon to 0.05% at the stage of liquid steel ladle treatment. It is also recommended to keep the titanium content in this type of steel not less than 0.3 % within the permissible composition according to *GOST 5632-2014*.

In case of defect detection in the metal structure at the stage of input control, it is necessary to carry out the austenization operation of steel at temperatures specified by thermodynamic calculation for an exact composition, and amounting to about 1,050–1,100 °C.

### *Study of the causes of the martensitic α-phase formation*

Metallographic analysis of the martensitic *α*-phase was carried out on samples of *12-Cr18-Ni10-Ti* steel rods obtained after the drawing stage. Samples with varying degrees of this defect manifestation were studied, technological parameters of cold forming were recorded in parallel.


*Fig. 2.* Occurrence of martensitic α-phase in steel *12-Cr18-Ni10-Ti*, rod Ø4 mm

Calculations show that in stainless steel of this type, martensite is formed at negative (Celsius degrees) temperatures, therefore its origin is most likely by deformation mechanism. Figure 2 shows an example of the martensite, formed by this mechanism in a metallurgical semi-finished product.

Measurements of the metal hardness show that a significant hardening follows the presence of martensite in the structure – the samples have a hardness of about 370 HB. Such values correspond to increased reduction of steel during the manufacture of rods. The analysis of technological parameters showed that with reduction of more than 50 % in the process of manufacturing a semi-product, there is an excessive amount of martensitic α-phase.

Thus, the appearance of this defect in rods made of *12-Cr18-Ni10-Ti* steel is associated with the stage of cold forming and is possible when the critical reduction of the billet is exceeded. During its formation, an additional step of metal austenization is required.

### *Investigation of the ferrite δ-phase in 12-Cr18-Ni10-Ti steel*

Samples of different thickness were studied to investigate the causes of the δ-phase formation in *12-Cr18-Ni10-Ti* steel. Figure 3 shows an example of the rod microstructure with a diameter of 3 mm in the direction of drawing.

Thermodynamic calculations show the presence of a ferrite phase in a wide temperature range from 1,250 to 1,450 °C, depending on the specific composition of steel, in particular the content of carbon, chromium, titanium and other elements. This range can be reduced by decreasing the ferrite stabilizing chromium in steel and slightly increasing carbon within the limits of allowable composition (but not higher than the value recommended for eliminating intergranular corrosion of 0.05 %) (Fig. 4).

In order to minimize the amount of δ-ferrite in the structure and remove excess magnetization, austenization is carried out – soaking at temperature of 1,050 °C. This temperature is outside the calculated range, however, even with such soaking, the ferrite phase does not completely dissolve for kinetic reasons. The residual particles of the δ-phase spheroidize and decrease in size.

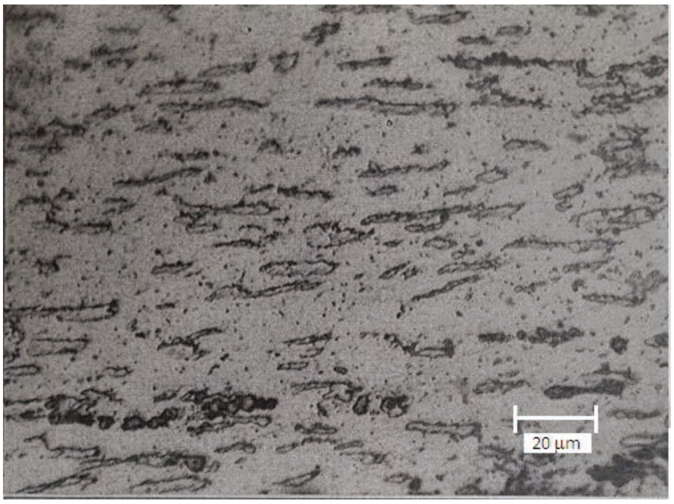


*Fig. 3.* Microstructure of a rod Ø 3 mm made of steel grade *12-Cr18-Ni10-Ti* after austenization

The results comparison of spectral analysis, metallographic studies and thermodynamic simulation show that the increased amount of ferrite phase in *12-Cr18-Ni10-Ti* steel corresponds to a wide calculated temperature range of its existence (about 200 °C). In the case of a shortened range (100 °C or less), the presence of ferrite is minimal and the magnetization is low. However, even in the case of high-

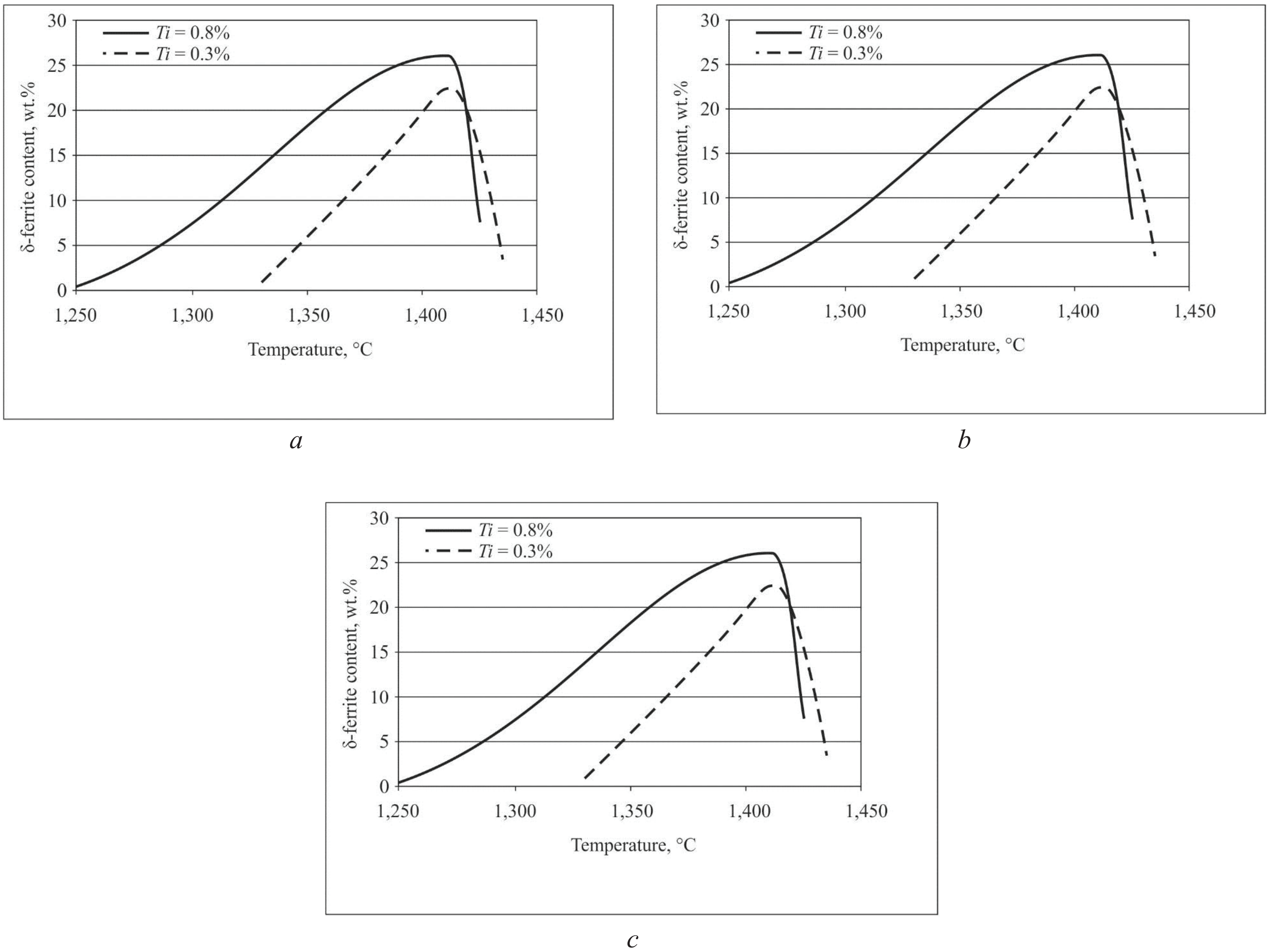


*Fig. 4.* Dependence of the content of δ-ferrite in steel *12-Cr18-Ni10-Ti* at different alloying contents:
*a* – the effect of titanium; *b* – the effect of chromium; *c* – the effect of carbon

temperature austenization, the *δ*-ferrite is not completely eliminated. Thus, to minimize the formation of this defect, optimization of the carbon and chromium composition, as well as austenization operation is required.

## Conclusion

As aim of the work, detailed studies of the reasons for defects formation in the microstructure of *12-Cr18-Ni10-Ti* stainless steel are carried out; such as intergranular corrosion, martensitic phase and δ-ferrite. Recommendations for its elimination are formulated based on the results obtained and thermodynamic calculations.

It is recommended to reduce the nitrogen and carbon content to 0.05% by methods of ladle liquid steel treatment to minimize the amount of $Cr_{23}C_6$ chromium carbides and, consequently, to increase the resistance of steel to intergranular corrosion. It is necessary to have titanium in steel at least 0.3% in accordance with *GOST 5632-2014*.

Required reduction should be not more than 50% in order to prevent the formation of deformation martensite in stainless steel during cold drawing.

In addition, it is recommended to optimize the chemical composition for chromium and carbon to reduce the temperature range of ferrite formation in order to avoid the presence of an excessive high-temperature ferrite phase in the structure.

In all three cases, the operation of billets austenization in the temperature range of 1,050–1,100 °C is appointed.

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## Conflicts of Interest

The authors declare no conflict of interest.