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# Transformation of structure and properties of structural steel during nanomodification and strengthening treatment

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The state of the problem of structure transformation and increase of mechanical properties of low-alloyed structural steels was investigated. The effect of hard-melting nanodispersed Ti(CN) particles on the structure formation of Si–Mn grain-refined steels was studied. Nanodispersed powder compositions of Ti(CN) with a fraction up to 100 nm were obtained by the method of plasma-chemical synthesis. The use of nanodispersed Ti(CN) compositions with a size of 50 nm as modifiers for structural steels 09G2 and 09G2C has been proposed and theoretically substantiated. The specified optimal amount of nanodispersed modifier Ti(CN) for processing structural steels 09G2 and 09G2C is 0.10 % of the mass. The grain refinement of castings in 2.0–3.5 times and grinding of ferritic-pearlitic structure of structural steels was achieved. Nanodispersed powder of titanium carbonitride Ti(CN) with a fraction from 50 to 100 nm was obtained by the method of plasma-chemical synthesis, and the technology of the modification process was developed. Severe plastic deformation of 09G2 and 09G2C steel castings was carried out. The structure, microhardness and properties of steels before and after treatments were studied. Grain refinement of steel and rise of yield point from 900 to 1250 MPa were achieved as a result of a combination of methods of hardening. An increase in strength characteristics of thermally unhardeneded steels can be achieved by reducing the grain size, strengthening the grain boundaries and the formation of submicrocrystalline structure or nanostructure. High-quality modified castings with a homogeneous structure were obtained. Severe plastic deformation and thermal strengthening (heat treatment) of steels were carried out. As a result of research it was found that the problem of transformation of grain structure and increase of mechanical properties of structural steels can be solved by application of highly efficient technologies: modification, development of rational thermal strengthening process and severe plastic deformation.

**Keywords:** structural steel, modification, nanodispersed modifier, structure, specific surface, severe plastic deformation, thermal strengthening, mechanical properties.

**Перетворення структури та властивостей конструкційної сталі під час наномодифікації та зміцнення.** *В.І.Большаков, О.В.Калінін, Д.Б.Глушкова, Ю.В.Рижков, В.А.Багров*

Вивчено стан проблеми перетворення структури та підвищення механічних властивостей низьколегованих конструкційних сталей. Досліджено вплив твердоплавких нанодисперсних частинок Ti(CN) на структуроутворення сталей, очищених зерном Si–Mn. Нанодисперсні порошкові композиції Ti(CN) з часткою до 100 нм отримано методом плазмохімічного синтезу. Запропоновано та теоретично обгрунтовано використання нанодисперсних складів Ti(CN) розміром 50 нм як модифікаторів для конструкційних сталей 09G2 та 09G2C. Зазначено оптимальну кількість нанодисперсного модифікатора Ti(CN) для обробки конструкційних сталей 09G2 та 09G2C становить 0,10 мас.%. Досягнуто очищення зерна у 2,0–3,5 рази та подрібнення феритно-перлітної структури конструкційних сталей. Методом плазмово-хімічного синтезу отримано нанодисперсний порошок карбонітриду титану Ti(CN) з часткою від 50 до 100 нм, розроблено технологію процесу модифікації. Проведено сильну пластичну деформацію виливків зі сталі 09G2 та 09G2C. Вивчено структуру, мікротвердість та властивості сталей до та після обробки. У результаті комбінації методів загартовування було досягнуто зернистість сталі та підвищення межі текучості від 900 до 1250 МПа. Підвищення характеристик міцності термічно незагартованих сталей можна досягти за рахунок зменшення розміру зерен, зміцнення меж зерен та утворення субмікрокристалічної структури або наноструктури. Отримано високоякісні модифіковані виливки з однорідною структурою. Проведено сильну пластичну деформацію та термічне зміцнення (термічна обробка) сталей. У результаті досліджень було встановлено, що проблема трансформації структури зерна та підвищення механічних властивостей конструкційних сталей може бути вирішена шляхом застосування високоефективних технологій: модифікації, розробки раціонального процесу термічного зміцнення та сильної пластичної деформації.

Изучено состояние проблемы трансформации структуры и повышения механических свойств низколегированных конструкционных сталей. Исследовано влияние тугоплавких нанодисперсных частиц Ti(CN)G на структурообразование сталей Si–Mn с измельченными зернами. Нанодисперсные порошковые композиции Ti(CN) с фракцией до 100 нм получены методом плазмохимического синтеза. Предложено и теоретически обосновано использование нанодисперсных композиций Ti(CN) размером 50 нм в качестве модификаторов конструкционных сталей 09G2 и 09G2C. Указанное оптимальное количество нанодисперсного модификатора Ti(CN) для обработки конструкционных сталей 09G2 и 09G2C составляет 0,10 мас.%. Достигнуто измельчение зерна отливок в 2,0–3,5 раза и измельчение ферритно-перлитной структуры конструкционных сталей. Методом плазмохимического синтеза получен нанодисперсный порошок карбонитрида титана Ti(CN) с фракцией от 50 до 100 нм, разработана технология процесса модификации. Проведена интенсивная пластическая деформация отливок из стали 09G2 и 09G2C. Изучены структура, микротвердость и свойства сталей до и после обработки. Улучшение зерна стали и повышение предела текучести с 900 до 1250 МПа достигнуты в результате сочетания методов упрочнения. Повышение прочностных характеристик термически незакаленных сталей может быть достигнуто за счет уменьшения размера зерна, упрочнения границ зерен и формирования субмикрокристаллической структуры или наноструктуры. Получены качественные модифицированные отливки с однородной структурой. Проведены интенсивная пластическая деформация и термическое упрочнение (термообработка) сталей. В результате исследований установлено, что проблема трансформации зернистой структуры и повышения механических свойств конструкционных сталей может быть решена путем применения высокоэффективных технологий: модификации, разработки рациональных процессов термического упрочнения и интенсивной пластической деформации.

## *1. Introduction*

The structural strength of materials plays an important role in ensuring reliable and long-lasting operation of machine parts and apparatus. The production of new equipment items in mechanical engineering and construction opens up more stringent requirements for the structure operability. This makes it necessary to use materials with a high complex of physical, mechanical and technological properties.

For metal materials, the problem of strengthening is associated with the implementation of new, environment friendly technologies, as well as improvement of existing technologies for the of rolled metal production for industrial and civil construction [1, 2].

At the same time, one of the most important requirements for steel used for critical metal structures is the level of strength, namely, high yield strength $\sigma_{0.2}$. This parameter is determined by structural indicators:

— grain size and structural components;

— presence and distribution of strengthening phases;

— phase interface type.

For high-strength structural steels, the problem of grain refinement and increasing strength is solved by applying highly efficient technologies, developing new steel compositions and rational thermal and mechanical treatment.

Therefore, the work aimed at studying the grain refinement processes of low-alloy structural steels and improving the strength properties is relevant and has scientific and practical interest.

Table. Chemical composition of low-carbon steels before and after modification

| Steel grade | Chemical elements, wt. %. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | Cr | Ni | Cu | S | P | Ti | N |
| 09G2, original | 0.12 | 0.40 | 0.90 | 0.30 | 0.30 | 0.30 | <0.040 | <0.035 | – | <0.004 |
| 09G2, modified | 0.14 | 0.44 | 0.95 | 0.25 | 0.25 | 0.15 | 0.028 | 0.030 | 0.035 | 0.008 |
| 09G2C, original | 0.12 | 0.42 | 1.02 | 0.30 | 0.30 | 0.30 | <0.040 | <0.035 | – | <0.004 |
| 09G2C, modified | 0.15 | 0.42 | 1.05 | 0.30 | 0.30 | 0.30 | 0.039 | 0.032 | 0.040 | 0.009 |

Silicon-manganese (Si–Mn) steels are used for important welded structures, including heavy-loaded ones: supports of multi-span railway bridges, tanks for petroleum products, as well as for oil and gas pipelines [2]. Along with static loads, they also are under dynamic loads.

The main alloying elements in low-alloy steels with up to 0.2 % C are manganese (Mn) (up to 1.8 %) and Silicon (Si) (up to 1.2 %). 09G2 and 09G2C steels belong to high-strength steels and correspond to C345 strength class with rolled thickness of 10 to 20 mm [3].

Complex-alloy steels containing vanadium or niobium correspond to a higher C355 and C375 strength class. However, the boundary between steel grades of different strength levels is blurred, which follows from notional (GOST 27772-88) and international standards (DIN 17102, ASTM370, ISO 19011) and International Translator of Steel Grades WinSteel ITSG.

Steels of this class are used for gas pipes under low temperatures. The advantage of Si–Mn steel is the increased impact strength [4]. There is also a tendency to reduce the carbon equivalent to improve the weldability of pipes. However, the use of steels with a ferrite-perlite structure is difficult due to the need to obtain, on the one hand, high strength (above X70 class), and on the other — low carbon equivalent. Therefore, the development of new, highly efficient methods of influencing steel melts through nano modification is one of the ways to solve the problem of improving the quality and strength properties of widely used low-alloy steels. In the domestic and foreign literature, there is information about the steel modification with either low-melting salts or scarce rare-earth dopants [4, 5]. There are no works on modifying Si–Mn steels with nanodispersed additives on industrial scale.

Low-alloy 09G2, 09G2C steels belong to two-phase ferrito-perlite steels, the structure of which consists of a fine-grained matrix of 15–20 % perlite. The structure of hardened steels also contains a small amount of residual austenite, bainite and dispersed carbides. To obtain a ferritic-martensitic structure, incomplete quenching is performed. The structure consists of 20 % martensite and 80 % ferrite.

Ferrite-perlite steels are not significantly strengthened by heat treatment. Improving the strength characteristics of steels without thermal hardening can be achieved by reducing grain size, strengthening grain boundaries, and submicrocrystalline or nanostructure forming. At the same time, it is possible to obtain such structural conditions when these factors can make a total contribution to increasing strength, for example, during the alloy modification with dispersed compositions.

## 2. Experimental

The aim of the paper is to study methods for grain refinement and increasing the strength properties of 09G2, 09G2C structural steels as a result of modification with nanodispersed compositions, heat-strengthening treatment and intensive plastic deformation.

Paper objectives:

— study of the structure and properties of low-alloyed steels in the original state;

— justify the choice of the nanodispersed modifier composition;

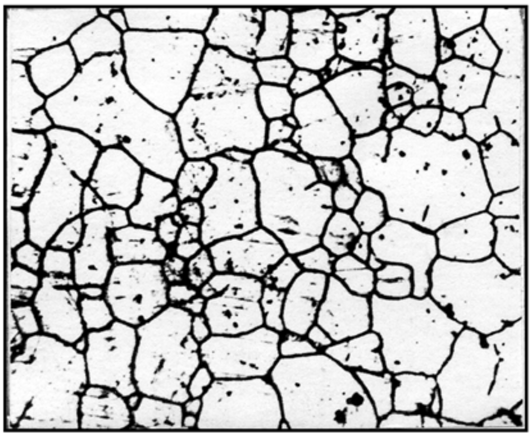
— select a method of obtaining nanopowders with specified crystallographic parameters;

— carry out severe plastic deformation of workpieces and thermal strengthening.

The research material was structural low-carbon 09G2, 09G2C steels. The chemical composition of the studied steels is shown in Table.

Various methods for nanopowder producing are known:

— gas phase synthesis;
— plasma chemical synthesis;
— thermal decomposition;
— mechanical action [7].



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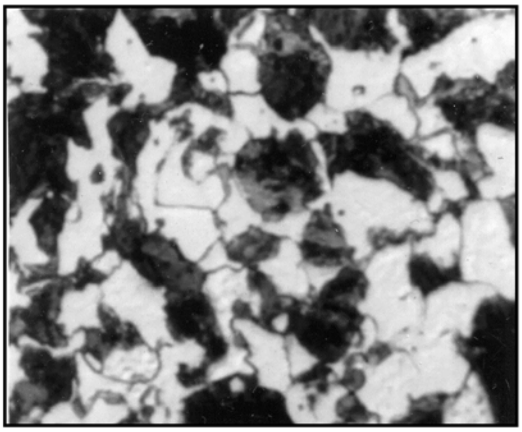

b

Fig. 1. Structure of austenite grains (a) and pearlite colonies (b) in silicon-manganese source steel, ×100.

### 3. Results and discussions

An increased content of carbon, titanium, and nitrogen was found in the modified steels, confirming the effect of nanopowder treatment. Titanium carbonitride modifier powder Ti(CN) with a particle size of 50–100 nm, was obtained by plasmochemical synthesis using high-frequency discharge plasma [6]. The raw material was industrial titanium powders with the size of ~ 200 um. The process was performed in nitrogen plasma. The carbon source was natural gas. At temperatures above 1000 K there was a transition of starting materials into the gaseous state, their interaction and condensation of products in the form of nanopowders with a given composition and crystallographic parameters. Titanium carbonitride nanoparticles had a face-centered cubic lattice [6].

The process of modifying the parameters of steel melts of geometric shape was performed during the manufacture of steels 09G2 and 09G2C in an induction furnace. The modifier, consisting of nanopowders Ti(CN) and steel powder, was compressed into tablets with a diameter of 25 mm, which were then immersed in the bottom of the ladle while stirring the melt. The amount of modifier was 0.1...0.2 % of the melt weight. After a short holding time (5...10 min) the modified melt was poured into metal molds for sample making. Modified workpieces were subjected to intensive plastic deformation and heat-strengthening treatment according to the mode: heating temperature 1050°C, holding time 5 min; cooling medium: water and 20 % solution of NaCl in water. Then the tempering was carried out at temperatures of 500°C; 600°C, the holding time was 30 min.

Metallographic studies of steel structure grains before and after modification were performed, as well as mechanical tests of standard samples on the TIRAtest 2300 Universal Machine.

In this paper, plasma chemical synthesis is chosen to produce high-melt compositions of titanium carbonitride. Only this way, the nanopowders of the same shape and crystallographic parameters can be obtained.

The nanoparticle size determines the properties of the nanodispersed system. The method of plasmochemical synthesis is based on high rates of volumetric condensation of the gas-flame flow, which leads to the formation of nanodispersed particles of titanium carbonitride fraction of 50...100 nm [6]. The resulting nanodispersed powders have distinctive features in comparison with massive powders: small parameters of the crystal lattice, high specific surface area of particles, the presence of amorphous formations. However, the available data are contradictory [3, 7, 14], especially at particle sizes of 20...50 nm.

The experiment was performed using Ti(CN) particles with a specific surface area of 2.0·105 $m^2$/kg. At such maximum specific surface area, the particles have the high adsorption capacity, and the seed domain crystalization on their surface is most likely [8, 9]. However, the "particle-crystallizing phase" formation is stable only if the free energy of the system decreases. The presence of a high specific surface area makes the process of the phase seed domain crystallizing energetically and thermodynamically advantageous. The process pro-

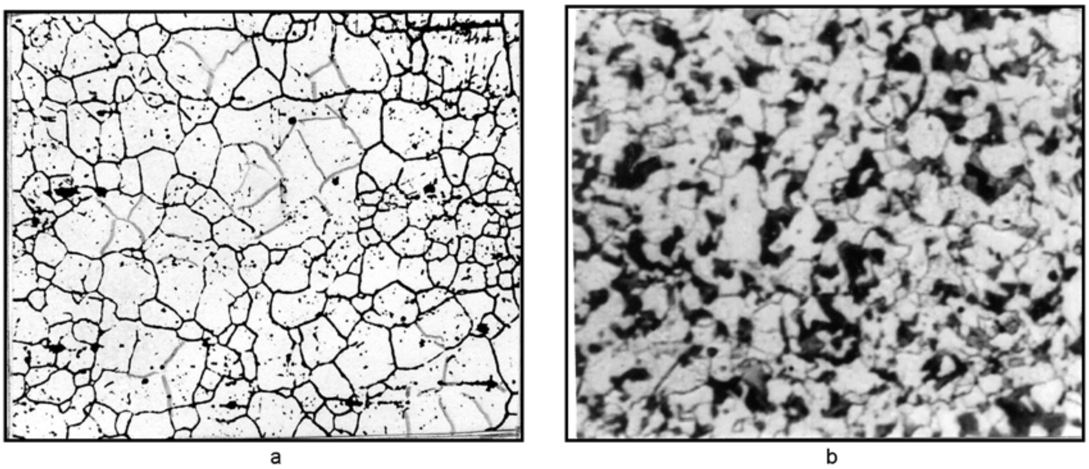


Fig. 2. The structure of austenite grains (a) and pearlite colonies (b) in silicon-manganese steel 10G2C after normalization, ×100.

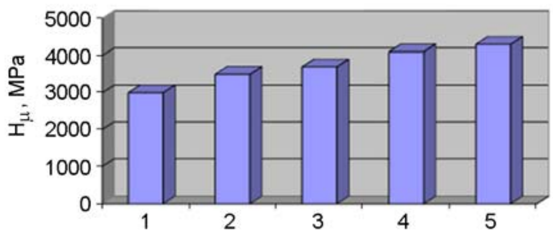


Fig. 3. Microhardness of 09G2C steel after modification; plastic deformation and cooling at different speeds: *1* — original state; *2* — cooling in water; *3* — cooling in NaCl solution; *4* — modification; *5* — plastic deformation.

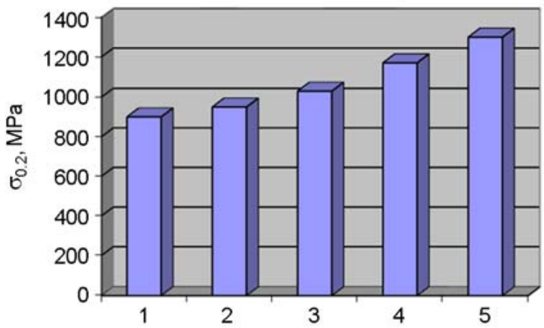


Fig. 4. Change in the yield strength of 09G2C steel after modification; plastic deformation and cooling at different speeds: *1* — original state; *2* — cooling in water; *3* — cooling in NaCl solution; *4* — nanomodification; *5* — plastic deformation.

ceeds with the energy release of latent crystallization heat. Thus, the solid phase on the surface of the particle is in an energetically favorable state. These iron-carbon melt sites, after subsequent cooling, have advantages over other sites without the modifier. Therefore, the grain size of modified alloys is determined by the number of particles introduced: the more of particles, the finer grain of primary austenite.

The role of nanodispersed additives is reduced to the creation of additional artificial crystallization centers in the melt [8, 9]. They must correspond to critical seed domain radii. For refinement of primary austenite grain in castings, the size of the introduced particles should be 40–50 nm.

The original and modified castings of 09G2 and 09G2C steels were subjected to intense plastic deformation by equal-channel angular pressing, followed by low-temperature annealing at the temperature of 350°C during 1 h [14].

In the original state, cast 09G2 and 09G2C steels had a ferritic-perlite structure with the average primary austenite grain size of 30 μm, after modification and deformation, the grain size was 10 μm (Fig. 1).

Figure 1 shows the microstructure of the source steel 09G2C (a, b).

After normalization (Fig. 2), nanomodified steel 10G2C is characterized by a smaller (2.0–3.5 times) austenite grain and a more dispersed homogeneous ferritic-pearlitic structure.

After quenching and cooling in water, the structure changed slightly to ferritic-troostite, with the average grain size of ~ 8...10 um.

After cooling the hardened samples in a 20 % NaCl solution in water, the structure of batch martensite was obtained. In the original state, the studied steels do not have sufficiently high properties: microhardness

*H*μ up to 3000 MPa, yield strength $\sigma_{0.2}$ up to 800 MPa.

During quenching in water, the hardness increases slightly, the most significant increase is observed when the samples are cooled in NaCl solution. Due to the significant refinement of martensitic crystals, the accelerated cooling gives a greater increase in hardness (Fig. 3).

Fig. 4 shows the data obtained as a result of plastic deformation of modified samples with a fine martensite structure. This leads to a further increase in microhardness and yield strength. After plastic deformation, the deformation texture appears.

## *4. Conclusions*

The study of the grain structure of 09G2 and 09G2C steels in the original condition showed the presence of the large grain up to 30 μm, reduced microhardness and yield strength.

The choice of the type and fraction of the nanodispersed modifier is justified. The use of plasmochemical synthesis for the production of titanium nanopowders is justified. Nanopowders of titanium carbonitride Ti(CN) fraction of 50...100 nm were obtained by plasma chemical synthesis. The chemical composition of nanocompositions is determined.

The technology for introducing a modifier into the steel melt has been developed. High-quality modified castings with uniform structure were obtained. Intensive plastic deformation and heat-strengthening treatment of steels was carried out. The modified steel had the grain size 3 times smaller than the original one, increased microhardness (up to 4000 MPa) and yield strength (1250 MPa) compared to the original one. Thus, the following methods are proposed for grain refinement and increasing the strength properties of steels: nanomodification, intensive plastic deformation in combination with heat-strengthening treatment.

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