Раздел третий

ФИЗИКА РАДИАЦИОННЫХ И ИОННО-ПЛАЗМЕННЫХ ТЕХНОЛОГИЙ

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STRUCTURAL MATERIALS MODIFICATION DURING PLASMOCHEMICAL SYNTHESIS ENRICHED WITH NANOPARTICLES

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The chemical composition of nanodispersed compositions was determined: SiC, TiC, TiN, Ti(CN), AlN, Mg_2Si, Mg_3N_2. The chemical composition of the synthesized compounds corresponded to the stoichiometric composition. An analysis of particles microdiffraction patterns was carried out, it was shown that nanopowders belongs to solid crystalline bodies with a metallic bond. It has been established that Ti(CN) titanium carbonitride particles are face-centered, and silicon carbide (SiC) have a hexagonal crystal lattice. Experiments on the surface modification of steels with nanopowder compositions based on Ti(CN) and SiC have been carried out. The effectiveness of using nanodispersed compositions in the smelting of structural steels has been established. As a result of the 09G2S steel modification with Ti(CN) nanopowder, the strength, plastic properties and toughness were increased. The choosing of nanodispersed Ti(CN) carbonitride powders with a fraction less than 100 nm as modifiers of low-alloy steels was substantiated. The necessary criteria for the selection of nanopowder modifiers were obtained: insolubility in melt, conformity of the crystal lattices with the matrix of steel, proportionality with the critical radius of the austenite nucleus during crystallization. The mechanism of a steel melt interaction with a layer of a nanodisperse composition was determined.

INTRODUCTION

Analysis of materials science scientific works of the last decade reveals that the researchers are focused on researching of the materials containing nanosized structural elements. Nanostructured material is the special condition of substance matters condensed phases – macroscopic ensemble of particles dimensioned in few nanometers. Exotic properties of these materials are derived from specific particles unusual properties and their chemical interaction type.

An effective technique of high-quality products production is the modification of steels with nanodispersed materials at their low consumption. Therefore, engineering solutions in the selection of nanodispersed compositions are based on the determination of the optimal complex of their parameters, composition, physical and mechanical properties and production technology.

In the light of the uniqueness of the properties of nanocrystalline materials that combine high strength and ductile characteristics, studies aimed at developing the technology of modifying processing of high-quality structural steels, nanodispersed compositions of a specified composition, crystal structure and dimensional-topological parameters should be considered actual.

HISTORICAL ANALYSIS AND TARGET SETTING

The development of new materials and technologies for their production is widely recognized as the basis of economic development. One of the priority development fields of materials science development is nanomaterials and nanotechnologies. Structural nanostructured materials occupy a special place among materials with the structure and property features [3, 4, 6–8]. The use of coarse particles of modifiers larger than 10 μm in the metallurgy of steel production has been sufficiently studied [1]. However, a small amount of scientific works are devoted to use of nanodispersed particles for steels structuring. Thus, in [9], when modifying low-alloy steel with refractory compositions, the formation of dispersed structures with a homogeneous distribution of strengthening phases was detected. However, it should be noted that in this scientific work a thermodynamic analysis of the modifying processes conditions at crystallization of melts has not been performed. In this regard, there are difficulties in choosing the optimal component composition and the size range of the nanocomposites used. This is due to the fact that the nanoparticles introduction into the melt essentially changes the surface phenomena at the “modifier-melt” boundary and the thermodynamic parameters of the process.

To solve this problem, an evaluation of the effectiveness of nanoparticles in the treatment of melts was performed in [5]. The dependence of the solubility level of the modifier in the melt on the thermodynamic stability of the process and the difference in the melting temperatures of the nanoparticles and melt is determined. Despite the practical value of the data presented, the features of the crystallographic structure of nanocomposites have not been adequately considered.

Therefore, the weight of evidence suggests that insufficient study of the influence of thermodynamic conditions and the crystallographic structure of nanocomposites necessitates research in this direction.

PURPOSE AND OBJECTIVES OF RESEARCH

The purpose of the research is to increase the mechanical and working properties of structural steels by modifying melts with nanodispersed compositions with specified crystallographic parameters.

In the furtherance of this goal the following tasks were accomplished:

– obtaining of carbide, nitride and carbonitride compositions with a particle size of up to 100 nm at plasmochemical synthesis production system;

– determining the chemical composition, physical properties and crystallographic parameters of nanoparticles;

– performing experimental-industrial melting of low-alloy steels of strength classes C345, C355, C375 with the use of nanomodifiers;

– determination of the effect of the specified crystallographic parameters of nanoparticles on structure morphology, the complex of mechanical properties, and the wear resistance of structural steels.

TEST MATERIALS AND EQUIPMENT

Modification studies were performed with the structural low-alloy steels using nanodispersed modifiers of TiC, TiN, Ti(CN), SiC, AlN, Mg_2Si with a particle size of 30…100 nm. The modifiers were produces using the high-frequency plasmochemical synthesis production system AEROXIDE P-25 at “Neomat” AO (Latvia).

Vortex induction plasmatrones with gas discharge stabilization were used to generate the plasma. The basic materials were dosed into the nitrogenous plasma flotation zone at a temperature of 5.500…7.500 °C. The heating, melting and evaporation of the basic materials as well as their chemical interaction were performed [2].

The size and crystallographic structure of the nanocomposites were studied using an EM-125 transmission electron microscope with a magnification of 100.000 and a DRON 2.0 diffractometer in Cu radiation.

Melting and modifications of steels were performed using the industrial induction furnace CAT with a capacity of 100 kg at temperature up to 1.600 °C. Castings were deformed on a thin sheet mill with a deformation degree of 40%. Tensile tests were performed using a tensile testing machine ЦД-4 and standard samples according to GOST 1497-84. The impact strength was determined on an impact testing machine according to GOST 9454-80.

DETERMINATION METHOD FOR STRUCTURAL STEEL PROPERTIES PARAMETERS

Evaluation of the effect of modifiers on the working properties of the steels tested was performed using the abrasion resistance method using the СМЦ-2 abrasion test machine and calculation of loss of the mass of the original sample of unmodified steel 09G2S.

The main parameters of the steels properties determined in the experiment are: temperature, time, modifier impregnation depth and modifier composition, %.

The main parameters of the physical and mechanical properties are: tensile strength, yield point, relative elongation, relative reduction and impact strength. The main parameters of the crystallographic parameters are the lattice constants (*a*, *c* in Å).

THE RESULTS OF RESEARCH ON THE PROPERTIES OF NANODISPERSED COMPOSITIONS AND STRUCTURAL STEELS TREATED WITH MODIFIERS

The chemical compositions of nanodispersed compositions produced at the plasmochemical synthesis production system are given in Tabl. 1.

Table 1

The chemical compositions of nanodispersed compounds synthesized

Material name	Elements content, mas.%									
	Si	Si free	C	C free	N	Al	Al free	Ti	Ti free	Mg
SiC	60…65	1.0…2.0	30…32	2.0…2.2	0.5…1.0	–	–	–	–	–
AlN	–	–	–	–	30…33	60…65	0.5…2.0	–	–	–
TiC	–	–	18…21	1.0…1.5	–	–	–	76…80	1.0…1.5	–
TiN	–	–	–	1.0…2.0	20…23	–	–	75…78	1.0…1.5	–
Ti(CN)	–	–	15…17	0.5…1.0	19…22	–	–	60…65	0.5…1.0	–
Mg_2Si	33…36	1.0…2.0	–	–	1.0…2.0	–	–	–	–	63…65

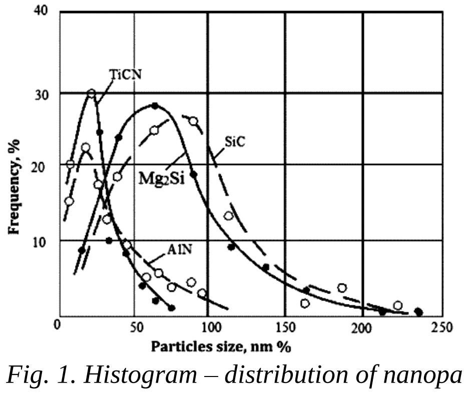

Fig. 1. Histogram – distribution of nanoparticles Ti(CN), AlN, SiC, Mg_2Si

It should be noted that the basis of all the compositions studied are elements (Al, Ti, Mg) forming chemical compounds. The contents of free elements are not significant (up to 20%).

The dimensional distribution of compounds nanoparticles at plasmochemical synthesis is shown at Fig. 1.

It should be noted that the Ti(CN) particles are characterized by the smallest size range (10…70 nm), while the largest range of sizes is shown by TiC particles (10…250 nm). Due to the data obtained, a conclusion can be drawn that the particles size distribution is asymmetric. Particles with the greatest density (Ti(CN)) (Tabl. 2) are of the size to 100 nm, and the particles with lower density (AlN and SiC) are of larger size – 150…200 nm.

Summarized results of nanodispersed materials crystallographic and physical properties research are given in Tabl. 2.

RESULTS AND DISCUSSION

Analysis of powders crystallographic parameters, electron microscopic images of particles and their microdiffraction patterns shows that finely dispersed compositions artificially created by plasmochemical synthesis belong to solid crystalline substances (Fig. 2). SiC and Ti(CN) saved their self-faceting ability and presents discrete three-dimensional system. Synthesized particles self-faceting ability is a consequence of their internal crystallographic structure, due to which the atoms of the crystal particles are located on certain straight lines and planes of crystallites. This was facilitated by the volume condensation of the plasma gas during the plasmochemical synthesis, allowing the particles to have a free crystallizing surface, which is confirmed in [10–12].

The microdiffraction patterns analysis of silicized carbon crystals made it possible to determine that due to their crystalline structure they belong to a hexagonal syngony with the following parameters: $a = 3.08$ Å, $c = 10.04$ Å. From the theoretical perspective, it can be assumed that the faceting of particles tends to provide the maximum surface energy with the minimum dimensions.

Electron microscopic analysis of Ti(CN) particles showed that the particles have a face-centered cubic lattice with the parameter $a = 4.25$ Å which is consistent with the data obtained for TiC ($a = 4.319$ Å) and TiN ($a = 4.243$ Å) [13].

Table 2

Crystallographic and physical properties of nanodispersed compositions

Material name	Dimensional-geometric shape of particles	Phase type	Lattice constant, Å		Density, kg/m^3	Melting (decomposing) temperature, ºC	Specific surface area, m^3/g
			a	*c*			
SiC	Hexagonal, trigonal	Interstitial	3.080	10.04	3.220	2.830 Decomposition	54.8
AlN	Hexagonal	Interstitial	–	–	2.350	2.200 Melting	64.6
TiC	Cubic	Interstitial	4.319	–	4.920	3.140 Melting	24.7
TiN	Cubic	Interstitial	4.243	–	5.430	2.950 Melting	21.6
Ti(CN)	Cubic	Interstitial	4.256	–	4.950	3.120 Melting	24.0
Mg_2Si	Cubic, spherical	Substituting	6.338	–	2.920	1.170 Decomposition	42.8

Comparison of measured and calculated Ti(CN) interplanar distance at diffraction patterns showed that Ti(CN) lattice is titanium carbon-based (TiC) and the nitrogen atoms are in positions of carbon atoms, forming a solid solution by nitrogen substitution in the crystal lattice of titanium carbon.

Thereunder, Ti(CN) particles have cubic or tetragonal shape. This is indicated by crystal projections configurations with their orientation [001], [111], [110]. The clear linearity cubes projections sides indicates the high perfection of the planes and edges of Ti(CN). The data obtained if consistent with the data of [13, 14].

In [9–13, 15] it is noted that the production of plasmochemical nanodispersed powders is due to high rates of volume condensation of the gas-flame flow, which leads to an nanodispersed particles unstable state.

Previous theoretical and experimental studies [5] showed that in order to achieve a low-alloy steels fine structure, the required amount of crystallization centers of austenite sized 30…50 nm in the melt should be $10^5…10^8$ pcs/cm^3. This corresponds to a consumption rate of 0.08…0.15% of the nanomodifier weight from the weight of the melt.

An effective technique of producing the structural steels with a fine structure and a high complex of mechanical properties for building structures of nuclear engineering is the modification of melts by refractory nanodispersed titanium-based compositions. The most effective modifier is titanium carbon Ti(CN) sized 30…50 nm. This refractory composition has face-centered cubic lattice similar to austenite face-centered cubic lattice and corresponds to low-alloy steels dispersed structure formation.

The mechanical properties of samples cut from deformed rods, after heat-hardening of pilot batches of 09G2 and 09G2C steels before and after modification are given in Tabl. 3 (the results are average of properties values of 7 specimens).

When considering the array of mechanical testing data, it was found that steels strength and plastic properties are improved, as a result of the modification by nanodispersed Ti(CN): $\sigma_в$ increased in average by 23%; $\sigma_{0.2}$ – by 19%; δ – by 23%; ψ – by 6%. The most significant increase in impact strength is on average 39% compared to the unmodified condition. This demonstrates the modification effectiveness.

To assess the effect of nanopowders on the working properties of workpieces, studies were performed on the influence of the depth of impregnation by the steel melt of Ti(CN) and TiC nanopowders in the form of a coating on the inner surface of the mold-box, which forms the working surface of the mold during casting.

The uniformity of the powder mixture has a significant effect on the impregnation process. That is why mixtures of Ti(CN) and TiC powders were prepared with constant stirring of components in attritor for the achievement of uniform distribution [13]. The tendency of the steel melt and nanopowders to interpenetration was estimated from the depth of the impregnated layer on the workpieces working surface. Measurement values are given in Tabl. 4.

Analysis of the data in the table shows that the impregnation of the layer with Ti(CN) nanopowder mixed with Ti(CN) promotes depth increase of the composite layer compared to pure titanium carbon. Ti(CN) nanopowder has the biggest impregnation depth – 20…22 mm.

The results of research of the effect of the temperature of the metal casted and the holding time of the melt to the impregnation depth are given in Fig. 2.

Table 3

Influence of modification on mechanical properties of steels

Steel grade	Steel condition	Mechanical properties				
		$\sigma_{\text{в}}$, MPa	$\sigma_{0,2}$, MPa	δ,%	ψ, %	KCU, MJ/m^2
C345	Unmodified	574	512	19.0	40.6	0.58
C345	Modified	762	641	21.5	45.2	0.76
C355	Unmodified	7657	568	18.2	43.0	0.58
C355	Modified	8811	675	22.4	45.7	0.81

Table 4

Various compositions C345 and C355 steels impregnation depth

Test No.	Depth of impregnation, mm		
	Ti(CN), 100%	TiC, 100%	50% Ti(CN) + 50% TiC
1	18…20	15…17	17…19
2	17…19	13…15	15…17
3	16…18	13…15	15…17
4	20…22	15…17	17..19

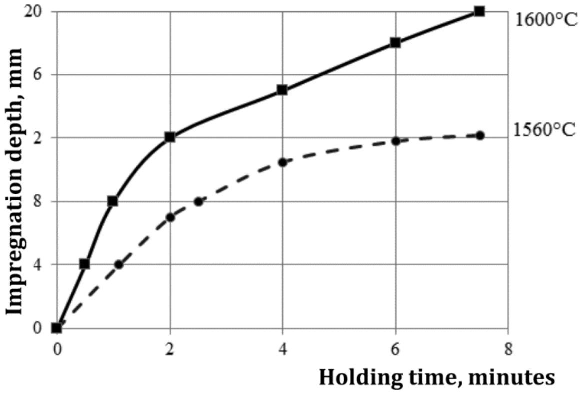

Fig. 2. The effect of the temperature of the metal casted and the holding time of the melt to the impregnation depth

Experiments proved that the heating of steel casted up to 1.600 °C and the holding time of the melt to 8 min significantly increases the depth of impregnation: Experiments proved that the significant increase of the impregnation depth can be achieved by heating of casted steel up to 1.600 °C with the holding time of the melt up to 8 min. According to test results, modified by Ti(CN) steel has the highest wear resistance. The wear resistance of the modified steel 09G2S is 2.5 times higher than the wear resistance of the original steel.

Modified steel 09G2S working properties testing results can be of significant practical importance allowing justifying the choice of the composition and the size and crystallographic parameters of the nanomodifier.

From a theoretical perspective, the experimental data obtained represent scientific novelty, which is: the mechanism of interaction of a steel melt with a nanodispersed composition layer is developed, which includes the following processes: heating of the nanopowder layer due to the sensible heat of the melt, melt filtration into the powder pores, nanopowder particles distribution in liquid-phase melt, diffusion processes under metal cooling. These results are the benefit of this research. However, it should be noted, that when justifying the selection of the modifier parameters and interpreting the mechanical properties of steels (see Tabl. 3), the structure changes of the modified steel is not taken into account. Such uncertainty places certain restrictions on the use of the obtained results, which can be interpreted as a weak point of this study. The inability to eliminate these limitations within the framework of this research substantiate the potentially interesting research area of further research. They can also aim on researching the relationship between the structure of impregnated steel layers and the temperature-time parameters of the process.

CONCLUSIONS

1. The performed investigations made it possible to determine the features of the crystallographic structure and physical properties of the nanodispersed compounds of the carbide, carbonitride and silicide class, which consist in conformability of the nanoparticles crystal lattice parameters with the steel crystal lattice. Due to this fact, it can be argued that it is the nanodispersed titanium carbonitride Ti(CN) that most effectively affects the modification process. This makes oneself evident in the fact that Ti(CN) particles serve as centers of crystallization, which make it possible to obtain the dispersed structure of steel, and, consequently, a high-quality of mechanical properties.

2. An analysis of the array of data on the mechanical properties of deformed workpieces revealed that the modification by titanium carbonitride increases $\sigma_{в}$ in average by 23%; $\sigma_{0.2}$ – by 19%; δ – by 23%; ψ – by 6%; 09G2 and 09G2S; the most significant parameter improvement is the impact strength increase (39%).

3. Due to the experiments performed, the mechanism of interaction of a steel melt with a nanodispersed composition layer was developed. Impregnation time-temperature parameters allowing achieving maximum layer depth at modification by Ti(CN) were determined.

4. The efficiency of nanodispersed compositions application in industrial conditions of production of structural steels with an increased complex of mechanical and working properties is determined.

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МОДИФИКАЦИЯ КОНСТРУКЦИОННЫХ МАТЕРИАЛОВ ПРИ НАСЫЩЕНИИ НАНОЧАСТИЦАМИ ПЛАЗМОХИМИЧЕСКОГО СИНТЕЗА

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Определен химический состав нанодисперсных композиций: SiC, TiC, TiN, Ti(CN), AlN, Mg_2Si, Mg_3N_2. Химический состав синтезированных соединений соответствовал стехиометрическому составу. Проведен анализ микродифракционных картин частиц, показана принадлежность нанопорошков к твердым кристаллическим телам с металлической связью. Установлено, что частицы карбонитрида титана Ti(CN) имеют гранецентрированную, а карбида кремния SiC – гексагональную кристаллические решетки. Проведены эксперименты по поверхностному модифицированию сталей нанопорошковыми композициями на основе Ti(CN) и SiC. Установлена эффективность применения нанодисперсных композиций при выплавке конструкционных сталей. В результате модифицирования стали 09Г2С нанопорошком Ti(CN) повышены прочностные, пластические свойства и ударная вязкость. Обоснован выбор нанодисперсных порошков карбонитрида титана Ti(CN) фракции менее 100 нм в качестве модификаторов низколегированных сталей. Получены необходимые критерии выбора нанопорошковых модификаторов:

нерастворимость в расплаве, соответствие кристаллических решеток с матрицей стали, соразмерность с критическим радиусом зародыша аустенита при кристаллизации. Установлен механизм взаимодействия стального расплава со слоем нанодисперсной композиции.

МОДИФІКАЦІЯ КОНСТРУКЦІЙНИХ МАТЕРІАЛІВ ПРИ НАСИЧЕННІ НАНОЧАСТКАМИ ПЛАЗМОХІМІЧНОГО СИНТЕЗУ

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Визначено хімічний склад нанодисперсних композицій: SiC, TiC, TiN, Ti(CN), AlN, Mg_2Si, Mg_3N_2. Хімічний склад синтезованих сполук відповідав стехіометричному складу. Проведено аналіз мікродифракційних картин частинок, показана належність нанопорошків до твердих кристалічних тіл з металевим зв'язком. Встановлено, що частинки карбонітриду титану Ti(CN) мають гранецентровану, а карбіду кремнію SiC – гексагональну кристалічні решітки. Були проведені експерименти з поверхневого модифікування сталей нанопорошковими композиціями на основі Ti(CN) і SiC. Встановлено ефективність застосування нанодисперсних композицій при виплавці конструкційних сталей. В результаті модифікування сталі 09Г2С нанопорошком Ti(CN) підвищені характеристики міцності, пластичності і ударна в'язкість. Обґрунтовано вибір нанодисперсних порошків карбонітриду титану Ti(CN) фракції менше 100 нм в якості модифікаторів низьколегованих сталей. Отримані необхідні критерії вибору нанопорошкових модифікаторів: нерозчинність у розплаві, відповідність кристалічних решіток з матрицею сталі, співмірність з критичним радіусом зародка аустеніту при кристалізації. Встановлено механізм взаємодії сталевого розплаву з шаром нанодисперсної композиції.