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Titanium-based high-melting nanodispersed compositions obtaining and study

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Crystallographic characteristics of nanodispersed materials obtained by plasma-chemical synthesis were studied. Using industrial equipment for plasma-chemical synthesis the nanodispersed powders of high-melting carbide, nitride, carbonitride and silicide class compounds based on titanium, magnesium, aluminium, silicon were obtained. Technology for synthesis of powder fraction less than 100 nm was developed. The efficiency of nanodisperse compositions use in smelting of structural steels was determined. In the result of 10Г2С steel modification with Ti(CN) nanopowder properties may by notice ably enhanced. Elemental composition of nanodispersed composition was determined: SiC, TiC, TiN, Ti(CN), AlN, Mg_2Si, Mg_3N_2. The elemental composition of synthesized compounds corresponded to stoichiometric composition. Microdiffractional patterns of the particles were analyzed; it was shown that nanopowders belong to the solid crystalline bodies with metallic bond. It has been found, that titanium carbonitride Ti(CN) particles have face-centered crystal lattice, while silicon carbide (SiC) particles have hexagonal lattice. Experiments for steel 10Г2 and 10Г2С modifying with nanopowder compositions on base of Ti(CN) and SiC were carried out. The efficiency of nanodisperse compositions use in smelting of structural steels was determined. In the result of 10Г2С steel modification with Ti(CN) nanopowder strength, plastic properties and impact toughness were improved. The choice of nanodisperse titanium carbonitride Ti(CN) powders with 100 nm fraction for light alloy steels modifying was justified. The required criteria for choice of nanopowder modifiers were obtained: insolubility in smelt, correspondence of crystal lattice to steel matrix, commensurability with austenite germ critical radius in crystallizing.

Keywords: nanodispersed composition, modifying, plasma-chemical synthesis, structural steel, mechanical characteristics, crystallographic characteristics.

Исследованы особенности кристаллографических параметров нанодисперсных материалов плазмохимического синтеза. На промышленной установке плазмохимического синтеза получены нанодисперсные порошки тугоплавких соединений карбидного, нитридного, карбонитридного и силицидного класса на основе титана, магния, алюминия, кремния. Отработана технология синтеза порошков фракции менее 100 нм. Установлена эффективность применения нанодисперсных композиций при выплавке конструкционных сталей. В результате модифицирования стали 10Г2С нанопорошком Ti(CN) могут быть заметно повышены свойства. Определён 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 кристаллическую решетку. Проведены эксперименты по модифицированию сталей 10Г2, 10Г2С нанопорошковыми композициями на основе Ti(CN) и SiC. 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 решёток с матрицей стали, соразмерность с критическим радиусом зародыша аустенита при кристаллизации.

Отримання та дослідження властивостей тугоплавких нанодисперсних композицій на основі титану. *В.І.Большаков, А.В.Калінін, Д.В.Глушкова, І.Г.Кириченко, А.І.Воронков, Л.Л.Костіна.*

Досліджено особливості кристалографічних параметрів нанодисперсних матеріалів плазмохімічного синтезу. На промисловій установці плазмохімічного синтезу отримано нанодисперсні порошки тугоплавких сполук карбідного, нітридного, карбонітридного та силіцидного класів на основі титану, магнію, алюмінію, кремнію. Відпрацьовано технологію синтезу порошків фракції менше 100 нм. Встановлено ефективність застосування нанодисперсних композицій при виплавці конструкційних сталей. У результаті модифікування сталі 10Г2С нанопорошком Ti(CN) можуть бути помітно підвищені властивості. Визначено хімічний склад нанодисперсних композицій: SiC, TiC, TiN, Ti(CN), AlN, Mg_2Si, Mg_2N_2. Хімічний склад синтезованих сполук відповідає 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 кристалічну решітку. Проведено експерименти з модифікування сталей 10Г2, 10Г2С нанопорошковими композиціями на основі Ti(CN) і SiC. Обгрунтовано вибір нанодисперсних порошків карбонітриду титану Ti(CN) фракції менше 100 нм в якості модифікаторів низьколегованих сталей. Отримано необхідні критерії вибору нанопорошкових модифікаторів: нерозчинність у розплаві, відповідність кристалічних решіток з матрицею сталі, співмірність з критичним радіусом зародка аустеніту при кристалізації.

1. Introduction

The problem of manufacturing of tailor-made products (wear-resisting, hot-resistance, corrosion-resistant) for industry is connected with steel alloying by deficit metals: Mo, V, rare-learth metals, Nb [1]. Constructional nanostructural materials take a special place between materials with specific structure and characteristics [3, 4, 6–8].The use of large particles-modifiers more than 10 μm size in steelmaking is well studied [1]. One of the prior tendencies in the modern materials science development is nanomaterials and nanotechnologies. The use of nanodispersed particles for steel structure management is studied just in few works. Thus, in modifying [9] of low-alloyed steel by high-melting compositions, it has been detected the formation of dispersed structures with homogeneous distribution of strengthening phases. However, it should be noted, that work doesn't have thermodynamic analysis of parameters of modifying processes in smelting crystallization. That means that there are difficulties from practical point of view in choosing of optimal composition content and size range of used nanocompounds. It is connected with surface phenomena essential changes on the "modifier-smelt" boundary and thermodynamic process parameters changes because of nanoparticles addition.

To solve this problem the estimation [5] of nanoparticles action efficiency during the smelt's treatment was done. The dependence of modifier solubility degree in smelt on thermodynamic stability of process and difference of nanoparticles and smelt melt temperature were defined. Despite of practical value of presented data, features of nanocompositions crystallographic structure were not studied.

The purpose of work was to study a problem of obtaining high-melting nanodispersed compositions with tailor-made crystallographic parameters for structural steels modifying.

To reach the purpose the following objectives were solved:

— to obtain nanodispersed compositions of carbide, nitride and carbonitride classes with particles size less than 100 nm using plasmachemical synthesis industrial equipment;

— to define elemental composition, physical characteristics and crystallographic nanoparticles parameters;

— to conduct experimental-industrial 10Г2 and 10Г2С steels smelting with use of nanomodifiers;

— to define the influence of tailor-made crystallographic nanoparticles parameters on complex of structural steels mechanical characteristics.

Table 1. Elemental composition of synthesized nanodispersed compounds

Material	Element content, wt. %.									
	Si	Si free	C	C free	N	Al	Al free	Ti	Ti free	Mg
SiC	65	2.0	30	2.0	1.0	–	–	–	–	–
AlN	–	–	–	0.5	33	65	1.5	–	–	–
TiC	–	–	21	1.5	–	–	–	76	1.5	–
TiN	–	–	–	1.0	23	–	–	75	1.0	–
Ti(CN)	–	–	15	1.0	19	–	–	65	1.0	–
Mg_2Si	33	1.0	–	–	1.0	–	–	–	–	65

2. Experimental

Modifying was conducted on constructional low-alloyed 10Г2 and 10Г2С steels with use of nanodispersed modifiers: TiC, TiN, Ti(CN), SiC, AlN, Mg_2Si with particles size 20...100 nm. Modifiers were produced in Neomat JSC (Latvia) at high-frequency industrial equipment for plasma-chemical synthesis AEROXIDEP-25.

To generate plasma the vortex induction plasma torch with gas discharge stabilization was used. Initial materials were gradually injected in nitric plasma flow with temperature 5500–7500°C. Heating, melting, evaporation of the injected materials and their chemical interaction were conducted [2].

The study of size and crystallographic structure of nanocompositions was conducted with use of transmission electron microscope 3M-125 at 100000 times magnification and X-ray diffractometer DRON 2.0 with Cu-anode.

Smelting and modifying of steels were done in industrial induction furnace with capacity 200 kg at temperature 1600°C. Mechanical pull testing was done on standard samples according to GOST 1497-84. The impact toughness was determined by GOST 9454-80.

As key parameters of mechanical characteristics the following were selected: resistance to rupture, flow limit, percentage extension, contraction ratio, impact hardness. The key parameters of nanocompositions were: physical characteristics, specific surface area, and crystalline lattice distance.

3. Results and discussion

Elemental composition of nanodispersed compositions obtained at plasma-chemical synthesis industrial equipment is shown in Table 1. It should be mentioned, that in the base of all compositions are elements (Al, Ti, Mg), forming chemical compounds. The content of those elements in unbound state can reach 20 %. Character of size-distribution of nanoparticles compounds of plasma-chemical synthesis is shown on Fig. 1. It should be noticed that the smallest range of size-distribution has Ti(CN)(10...70 nm), and the biggest one — SiC (10...250 nm). Obtained data let us conclude that character of particles size-distribution is asymmetrical. Ti(CN) particles with biggest density (see Table 2) have average size less than 100 nm, and more light particles (AlN and SiC) have bigger size — up to 200 nm.

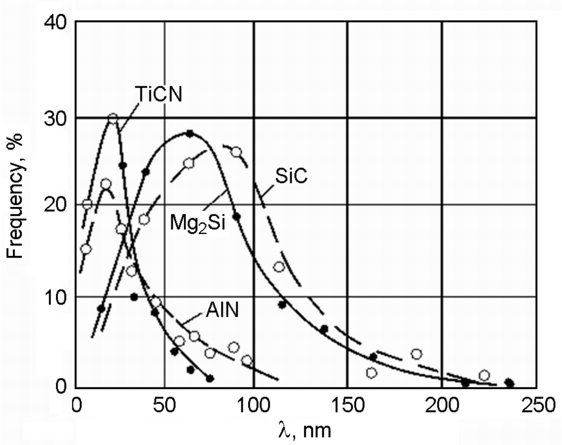

Fig. 1. Distribution charts of nanoparticles Ti(CN), AlN, SiC, Mg_2Si.

Summarized data of crystallographic and physical characteristics studies of nanodispersed materials is shown in Table 2. Analysis of powders crystallographic characteristics, particles electron microscopic images and their microdiffraction patterns show that finely dispersed composition artificially created with plasma-chemical synthesis belongs to solid crystalline compounds (Fig. 2). SiC, Ti(CN) saved their ability for self-faceting and represent discrete three-dimensional system. The ability of synthesized systems for self-faceting is a consequence of their internal crystallographic structure due to which atoms of crystal-particles are located on certain crystallite lines and planes. This contributed to

Table 2. Crystallographic and physical characteristics of nanocompositions.

Material	Crystal lattice	Phase type	Lattice distance, Å		Density, kg/m^3	Melting temperature (decomposition), °C.	Estimated specific surface area m^2/gm^3
			a	c			
SiC	Hexagonal, trigonal	Implementation	3.080	10.04	3220	2830 Decomposition	54.8
AlN	Hexagonal	Implementation	–	–	2350	2200 Melting	64.6
TiC	Cubic	Implementation	4.319	–	4920	3140 Melting	24.7
TiN	Cubic	Implementation	4.243	–	5430	2950 Melting	21.6
Ti(CN)	Cubic	Implementation	4.256	–	4950	3120 Melting	44.0
Mg_2Si	Cubic, spheric	Substitution	6.338	–	2920	1170 Decomposition	42.8

plasma gas volume condensation during plasma-chemical synthesis, which allows particles to have free crystallizing surface, which is confirmed in studies [10–12].

Analysis of microdiffraction patterns of silicon carbide crystals allowed to define, that by crystalline structure they belongs to hexagonal syngony with $a = 3.08$ Å, $c = 10.04$ Å parameters. SiC particles are forming in shape of hexagonal and trigonal prisms with low height (Fig. 2a, b). Analysis of contrast on SiC particle image demonstrates that it has smaller size on the periphery than in central part.

From theoretical point of view it can be considered that particles faceting is tending to provide maximum surface energy with their minimal sizes.

Electron microscopy Ti(CN) particles analysis has shown, that particles have face-centered cubic lattice with $a = 4{,}25$ Å parameter. This is consistent with the data for TiC ($a = 4.319$ Å) and TiN ($a = 4.243$ Å) [13].

Comparing of measured and pre-calculated interplane Ti(CN) distance on diffraction patterns showed that Ti(CN) lattice is built on base of titanium carbide TiC, nitrogen atoms are in octahedral interstitial sites forming solid solution of nitrogen substitution in titanium carbide crystal lattice.

According to it Ti(CN) particles are formed of cube or tetragons. This is indicated by crystals projections configurations during their orientation [001], [111], [110]. Distinct linearity of cubes projections sides is pointing on high Ti(CN) faces and edges perfection. Obtained data are consistent with studies data [13, 14].

Electron microscopic images of magnesium silicide Mg_2Si particles are showing non-spherical form of particles in face-centered cubic lattice. There are different opinions about Mg_2Si crystalline lattice type. According to the obtained data [15] Mg_2Si crystalline lattice is hexagonal.

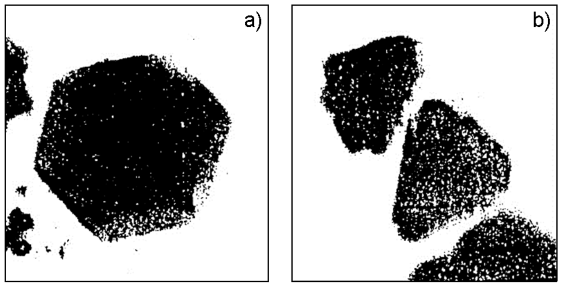

Fig. 2. Electron microscopic images of ultradispersed silicon carbide particles, ×100000. Prisms: a) hexagonal, b) trigonal.

Our calculations results shows that Mg_2Si interplane distances correspond to face-centered cubic lattice with $a = 6.338$ Å parameter (Table 2).

It is mentioned in [10–13, 16], that plasma-chemical nanodispersed powders obtaining is due to high rate of gas-fired flow volume condensation, which leads to nanodispersed particles unstable state.

The effective way to create finely dispersed structure and high complex of mechanical characteristics of structural steels is to modify smelts with high-melting nanodispersed compositions on base of titanium [2, 5, 11]. The titanium carbonitride Ti(CN) with 20–50 nm particles size is the most effective modifier. This high-melting composition has face-centered cubic lattice like austenite face-centered cubic lattice and promotes the formation of dispersed structure of structural steels.

Mechanical characteristics of samples cut from deformed rods, after thermo-harden-

Table 3. Modification influence on mechanical characteristics of 10Г2 and 10Г2С steels

Steel brand	Steel state	Mechanical characteristics				
		σ_v, MPa	$\sigma_{0.2}$, MPa	δ, %	ψ, %	KCU, MJ/m^2
10Г2	Unmodified	574	512	19.0	40.6	0.58
10Г2	Modified	762	641	21.5	45.2	0.76
10Г2С	Unmodified	657	568	18.2	43.0	0.58
10Г2С	Modified	811	675	22.4	45.7	0.81

ing treatment of experimental-industrial batches of 10Г2 and 10Г2С steels and after modifying are given in Table 3.

By revising of mechanical tests data set it was defined that in result of modifying with nanodispersed Ti(CN), strength and plastic steels characteristics are increasing: σ_v and $\sigma_{0.2}$ average increase is 20 %; δ — 23 %; ψ — 6 %. The most significant was the impact toughness increase averagely on 40 % in comparison to unmodified state. That proves the efficiency of modifying.

4. Conclusions

Special aspects of crystallographic structure and physical characteristics of nanodispersed compositions of carbide, carbonitride and silicide classes which are in correspondence between nanoparticles crystal lattice and steel crystal lattice parameters were determined. Due to that it's possible to assert that nanodispersed titanium carbonitride Ti(CN) has the most effective influence on 10Г2 and 10Г2С steels modifying process. This is manifested in the fact that Ti(CN) particles apparently serves as centers of crystallization allowing to obtain steel dispersed composition and thereby a high level of mechanical properties.

By analyzing structural steels mechanical characteristics data set it was defined that titanium carbonitride modifying increase strength and plastic characteristics averagely on 20 %; impact toughness has the biggest increase (on 40 %).

The efficiency of nanodispersed compositions use in industrial conditions production of structural steels with increased mechanical characteristics complex was determined.

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