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INVESTIGATION OF THE INFLUENCE OF NANODISPERSED COMPOSITIONS OBTAINED BY PLASMOCHEMICAL SYNTHESIS ON THE CRYSTALLIZATION PROCESSES OF STRUCTURAL ALLOYS

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Abstract

The state of the problem of stabilizing the structure, improving the quality and properties of structural alloys is studied. To solve the problem, it is proposed to modify melts of low-alloyed alloys with nanodispersed compositions obtained by plasma-chemical synthesis. Process technological parameters are developed. Nanopowders of carbide and carbonitride class SiC and Ti (C, N) with a size of 50...100 nm are obtained. The crystallographic parameters of the nanocompositions and the specific surface are determined, and the dependency curves are plotted. The macro- and microstructure of structural steels and alloys was studied before and after the modification. A significant (in 2...3.5 times) grain refinement and stabilization of the alloy structure as a result of nanopowder modification of titanium carbonitride have been achieved. Thermodynamic calculations of the dimensions of crystalline seeds during the crystallization of steels and alloys are carried out. A complex criterial estimation of the efficiency of nanodispersed compositions in a steel melt is proposed. The features of crystallization and structure formation of modified structural steels are studied. The obtained results are of theoretical and practical importance for production of critical parts from structural steels and high-quality alloys.

Keywords: structural steel, aluminum alloy, nanodispersed compositions, plasma-chemical synthesis, crystallization, structure.

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1. Introduction

The field of study of nanodispersed materials is the most rapidly developing in modern materials science, since the production of finely dispersed structures contributes to a fundamental improvement in the complex properties of structural steels and alloys. The development of nanotechnology is based on the use of physical-mechanical and surface properties of powder materials [1]. The main reason for the appearance of special surface properties of nanomaterials and nanosystems is the high specific surface area and energy activity of nanoparticles. Also, one of the main reasons is the role of size effects, which manifests itself both in individual nanoparticles and in nanosystems [3]. All this is reflected in the mechanisms of ordering of nanomaterials associated with the patterns of changes in their structure and physic-mechanical properties [2–6].

The acquisition of new nanomaterials is inextricably linked with the development of nanotechnologies, which provide the solution of the following problems [4, 6]:

– obtaining materials with a given structure and properties;

– study of the features of the surface properties and structure of nanodispersed compositions that contribute to hardening of structural materials.

2. Literature review

It is noted in [7, 8] that currently used structural steels and alloys do not provide the required durability of machine parts, since they have insufficient strength properties. In the technical literature [9, 10], ways to improve the quality and properties of steels through optimization of composition, microalloying, thermal and thermomechanical processing are considered. The most effective way of obtaining a disperse structure and a high level of strength is modifying [9]. There are several theories of modification, but none of them describes the process completely. Nanodispersed compositions have been used as modifiers of steels and alloys [10–13]. The disadvantage of the work on the modification of structural steels and alloys with nanodispersed compositions is the lack of a comparative evaluation of different methods for obtaining nanocomposites and the thermodynamic analysis of the existence of nanoparticles in the melt.

The aim of the work is refining the grain and stabilization of the structure of structural steels and aluminum alloys by treatment with nanodispersed compositions. This will improve the quality and strength properties of structural alloys, ensuring the required durability of machine parts.

Objectives of the research:

– to choose a method for obtaining nanodispersed compositions;

– to study the granulometric composition and parameters of refractory nanocomposites of the carbide and carbonitride class;

– to conduct a thermodynamic analysis of the crystallization of melts with nanoparticles;

– to study the structural features of steels and alloys modified with nanocomposites.

3. Materials and Methods

The materials of the study are structural low-alloy steels 09Г2С and 09Г2ФБ, these grades of steel are most widely used for the manufacture of parts and building structures, pipe products, as well as aluminum alloys Al-Mg for welded structures. To obtain nanodispersed powders of the fraction of less than 100 nm of pure metals (Ti, Cu, Si), their mixtures and refractory compounds (Ti (C, N), SiC), a high-frequency plasma chemical synthesis device is used [13–16]. The technological process of plasma-chemical synthesis is developed, which includes the following stages:

– preparation of raw materials;

– generation of a plasma jet;

– plasma-chemical synthesis;

– capture of the target product.

Titanium and silicon carbide powders (100...300 μm), obtained from waste from metallurgical and silicon-polymer industries, are used as raw materials. After drying, the powder components are mixed, loaded into the cylinders of a powder feeder, which ensures degassing of the mixture of powders and pneumo-transportation to a slice of the plasma torch [13, 17]. The granulometric composition and parameters of nanocompositions are studied by X-ray diffraction analysis and electron microscopy [4]. The structure of steels and alloys is studied by light microscopy [5].

4. Discussion of research results

Nanodispersed compositions are prepared by the method of plasmochemical synthesis. A high-frequency plasmatron with gas discharge stabilization was used to generate the plasma [12, 13]. In connection with the high ionization potential of nitrogen in the plasma torch, an argon discharge is created by means of an electric pulse of high voltage from a tungsten ignition needle. At the time of the electric discharge, an avalanche-like ionization of argon takes place. Then nitrogen enters the discharge chamber, and the supply of argon ceases. Cooling of the outer surface of the chamber is done by a directed air flow.

Synthesis of nanodispersed titanium boron nitride Ti (C, N) is based on the interaction of titanium, nitrogen and carbon vapors. A mixture of the initial powders is introduced into the zone of the nitrogen plasma flow with an average mass temperature of 5500...7500 °C. At the same time, heating, melting, evaporation of powders and their chemical interaction take place.

At the exit from the reactor, the temperature of the gas-powder flow is 1200...1400 °C. For an intensive reduction in the flow temperature, a heat exchanger system was used that provided a flow temperature of 100 °C at the outlet. From the heat exchangers, the cooled stream enters the trapping chamber, where the nanodispersed target product settles in the bag filters.

To obtain Ti (C, N) from metallic titanium, an effective heat carrier is necessary, as inert as possible with respect to the constituent elements. One of the features of plasma-chemical synthesis is the short-term interruption of the reagents in the reaction zone and the lack of the opportunity, in connection with the short duration of the process, to ensure a high degree of conversion of the raw material into the target product. Argon is used as coolants, which is used to ignite the plasma and nitrogen – to produce nitrogen plasma. The experiments are carried out in the following technological regime: anode power 72 kW, flow of plasma gas 8.5 m^3/g, flow of transporting gas 3.0 m^3/g. The mixture of the initial powders had the composition, % by mass: titanium – 60, nitrogen – 40.

Sampling for analysis is conducted from the reactor walls. X-ray phase, electron microscopic analysis and determination of the specific surface area of nanopowders are carried out. The specific surface is determined from thermal desorption of argon by chromatographic method [10].

The chemical composition of nanocompositions used as modifiers is given in **Table 1**.

Table 1

The chemical composition of synthesized nanodispersed compositions

The formula for compound	Content of elements,% wt.			
	Si	C	N	Ti
SiC	60–65	30–32	–	–
TiC	–	18–21	–	76–80
TiN	–	–	20–23	75–78
Ti(C,N)	–	15–17	19–22	60–65

The generalized results of crystallographic and dimensional topological studies of nanodispersed compositions are given in **Table 2**.

Table 2

Crystallographic and dimensional-topological parameters of nanodispersed compositions

The formula for compound	Crystal system	Phase type	Lattice period, Å		Density, kg/m^3	Melting point (decomposition), °C	Dimension, nm	Specific surface, m^2/g
			a	c				
SiC	Hexagonal	Intrusions	3,080	10,04	3220	2830	55,0	15,5
TiC	Cubic	Intrusions	4,319	–	4920	3140	80,0	14,0
TiN	Cubic	Intrusions	4,243	–	5430	2950	70,0	11,0
Ti(C,N)	Cubic	Intrusions	4,256	–	4950	3120	86,0	14,0

The transition of the material to the nanodispersed state with a decrease in particle size sharply increases the adsorption and catalytic activity of the system, since the surface fraction with respect to the total volume of the particles increases significantly. A sharp increase in surface energy in the transition of particles to the nanodispersed state and a change in the thermodynamic conditions of phase equilibria lead to the appearance in them of phenomena such as high-temperature superconductivity, a super-magnetic and amorphous state [19–21].

The most important task in the process of obtaining nanodispersed modifiers is to maintain a clean surface that provides a large adsorption and catalytic activity. Only in this case the particles introduced into the melt will play the role of active centers of crystallization.

The preparation of nanodispersed compounds (Ti (C, N), TiC, TiN, SiC) by the method of plasma-chemical synthesis is caused by high rates of volumetric condensation of the gas-flame flow, which already at the stage of formation leads to an unstable state of nanodispersed particles:

– nanodispersed powders are characterized by smaller parameters of the crystal lattice in comparison with massive samples of the same alloy;

– different types of amorphous formations take place;

– there is a decrease in the lattice parameters of particles from the center to the surface due to the maximum compression of the surface layer, which causes an inhomogeneous distribution of components and phases along the radius of the particle.

Dispersion of nanoparticles largely determines the properties of a dispersed nanosystem and is quantitatively characterized by linear dimensions and the specific surface area of the particles. The specific surface S_s is expressed by the equation:

$$S_{s=} S_{1-2}/\gamma V, \quad (1)$$

where S_{1-2} – the interphase surface between particle 1 and medium 2; γ – the density of the nanodispersed particle; V – the volume of the nanodispersed system.

Fig. 1 (curves 1–3) shows the change in the specific surface with a decrease in the surface of particles from coarsely dispersed particles (more than 10^5 nm) to systems of molecular degree of dispersion (less than 10 nm). Curves 1–3 have the form of hyperbolas. In the region of coarsely dispersed systems, the curves asymptotically approach the abscissa axis. In the region of the nanodispersed system (NDS), the curves rise sharply. Owing to the large specific surface area of nanodispersed systems, adsorption and surface phenomena are of great importance for them, while the behavior of coarsely dispersed systems is mainly determined by bulk properties [15].

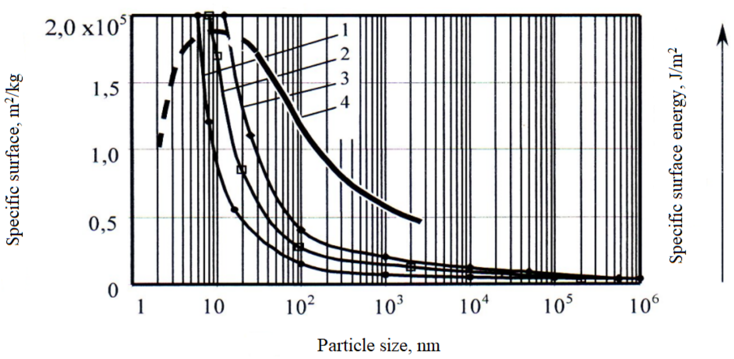

Fig. 1. The influence of the particle size on the specific surface area
(1 – TiCN, 2 – SiC, 3 – Mg_2Si), and the averaged surface energy

Curve 4 (**Fig. 1**) characterizes the dependence of the surface energy (SE) on the particle dispersion. It is seen that as the dispersion increases, SE in the region of the nanodispersed system increases. When the particles pass into the nanodispersed state, a sharp increase in the specific surface energy and a change in the thermodynamic conditions of phase equilibria occur. These processes lead to the appearance in nanodispersed systems of phenomena such as high-temperature superconductivity, a super-magnetic state, and a shift in the temperatures of phase transformations [16–18].

The process of structure formation of 09Г2С and 09Г2ФБ steels modified with nanodispersed compositions based on Ti (C, N), as well as an aluminum alloy of the Al-Mg system modified with silicon carbide SiC, is studied.

Nanoparticles commensurate with the crystallization centers have a high adsorption capacity and therefore nucleation in the crystallization of the primary phase (in this case, the shell) on their surface is highly probable. The formation (particle-shell-melt) will be stable, since the free energy ΔF of this system decreases [22].

If there is a refractory nanoparticle in the melt, the formation of a solid shell of the primary phase on its surface will be the same as in the formation of the center of the new phase. The change in the total free energy ΔF depends on the sum of the changes in the volume and surface free energies:

$$\Delta F = \sum \Delta F_v + \Delta F_s, \quad (2)$$

where ΔF_v and ΔF_s are the change in the volume and surface free energy of the system.

By changing the ratio of volume and surface free energies, nucleation of the primary phase on the nanoparticles present in the melt is facilitated, and proceeds with decreasing total free energy. While the formation of seed in an unmodified melt requires energy expenditure and becomes thermodynamically unprofitable.

The presence of a large specific surface area of the nanoparticle makes the process of nucleation of the solid phase on their surface thermodynamically advantageous in the absence of such tendency for decay. Such sections of the solid phase, when the melt is cooled to the crystallization temperature, win in competition with spontaneously or heterogeneously arising seeds. As a result, the size of grains in castings from modified steel and alloys is determined by the amount of nanoparticles: the more of them, the more dispersed grain.

Thus, the role of nanodispersed particles is reduced to the creation of additional artificial crystallization centers in the melt. In this case, they must be commensurate with critical embryos for mass input to produce a finely dispersed structure of steels and alloys.

Theoretical and experimental studies have shown that in order to achieve a finely dispersed structure of steels and alloys, it is necessary that in the melt there should be at least 105...108 pieces/cm^3 of crystallization centers with a size of 20...40 nm, which corresponds to 0.08...0.15 % of the introduced nanodispersed Ti (C, N) and SiC.

The investigated steel after modification is characterized by a smaller (in 2.0...3.5 times) austenite grain and a dispersed homogeneous ferrite-pearlite structure.

5. Conclusions

The obtained results are used in the development of technological recommendations and instructions for modifying low-alloy steels and aluminum alloys with refractory nanocomposites of the carbide and carbonitride class.

The preparation of nanodispersed compositions by the method of plasma-chemical synthesis is proposed. The technological process and optimal parameters of the temperature regime for obtaining nanopowders in nitrogen plasma are developed. The chemical composition of the obtained powders, crystallographic parameters and physical properties are given. The sizes of Ti (C, N) TiC, TiN and SiC powders, their specific surface area and specific surface energy are calculated. Conditions for the thermodynamic stability of the system are established under which nanoparticles are the centers of melt crystallization. The grinding of the grain of 09Г2С and 09Г2ФБ steels and aluminum alloys of the Al-Mg system is achieved as a result of modification in 2.0...3.5 times.

Based on the research results, a technological instruction is developed and recommendations are given to industrial enterprises for processing steels with nanodispersed modifiers.

The authors plan to expand the range of structural alloys of various alloying systems, as well as improve the parameters of the technological process of modification.

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