Production of new nanostructures for modification of steels and cast irons

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Abstract. Two new nanoscale materials from silicon wastes were developed. Carbon material consists of a mixture of amorphous nanoparticles with a maximum size distribution of 200-500 nm, aggregated coils of carbon nanotubes about 1% of the volume, globular nanoparticles of a spherical form of crystalline silicon dioxide with a maximum size of 200-300 nm, coated with a carbon shell with a wall thickness of 4-6 nm. Silicate material contains over 90-97% of amorphous silicon dioxide with a maximum size of 200-300 nm, and also contains silicate nanotubes representing silica with a diameter of 50-60 nm. It was determined that the mechanism for the modification of metals and alloys, obtained by nanostructured materials, is formed in accordance with the hypothesis of a local stress field at the ends of the tubes, increasing the rate of formation of the crystallization centers of the melt. An additional modifying effect is exerted by the large surface energy of nanostructured materials, if we compare them with modifying materials that have micron-sized structures.

1. Introduction
Recently, an increasing attention has been paid to the use of specially prepared refractory nanoparticles for the modification of steels and alloys in order to refine the structure of the cast metal [1-4]. It is shown that small additions of nanoparticles in the amount of hundredths of a percent by mass lead to a substantial refinement of the cast metal grain and to an increase of its mechanical and service characteristics. It was also found that the degree of assimilation and, correspondingly, modifying effect largely depend on the size and wettability of nanodispersed particles [1-4]. Therefore, study of the features of nucleation of crystallization centers on activated ultradispersed seeds (nanoparticles), considering the size and capillary effects, is of interest for constructing the theory of structure formation in alloys modified by highly disperse refractory compounds with dimensions of 0.01-0.1 μm.

2. Materials and methods of research
As a starting material for the production of new nanostructures, wastes from the production of silicon were chosen. Conditions, under which these wastes are formed, are of interest because the forming particles have already undergone high-energy treatment. Chemical and granulometric composition (high content of amorphous micro- and nanocrystalline SiO₂, carbon nanostructures, silicon carbide) makes it possible to use this raw material for a second time and reduce energy costs for obtaining nanostructures.

These advantages make the dust of silicon furnaces an attractive secondary raw material for the extraction of useful components and allow using it as modifiers in metallurgy, mechanical engineering and the construction industry. The following treatment scheme was chosen. Base material (sludge -
wastes of silicon production), preliminarily diluted in water and treated with reagents (foaming agents, collectors and depressors), was passed through a hydroacoustic cavitator.

Sludge treatment in the cavitator was carried out for the following purposes: 1) destruction of conglomerates of carbon particles with silica particles; 2) hydrophobilization of hydrophilized carbon particles; 3) depressions of silica particles with liquid glass (or other depressors). Fourth, there is also formation on the hydrophobic surface of particles of micro- and nanobubbles due to cavitation that subsequently contribute to the formation of floating flotocomplexes by coalescence with free bubbles and their increase due to the gas dissolved in water. After the pre-treatment, the resulting mixture entered the laboratory flotation machine. To investigate samples of sludge, foam and flotation tail, modifiers, metal samples and concrete samples, we used a scanning electron microscope JIB-Z4500. JEOL (manufactured in Japan) and a transmission microscope Tecnai™ G² F20 with excellent image formation characteristics in modes of TEM, STEM. There was nanoanalysis, ultrahigh vacuum, high spatial coherence, a complete sample preparation line, information limit of <0.12 nm and a power of 25x-1,000 kx (TEM) of 150x-230 Mx (STEM).

3. Research results and discussion
Conducted studies showed that the flotation process for extracting particles of such small dimensions should consider the following points. Particles with such small size are already subject to Brownian motion, therefore they are carried out through the tailboard by a conventional impeller flotation machine. Flotation of nanoscale particles should be carried out with nano-sized bubbles commensurate with them. Feedstock contains a significant amount of silicon dioxide aggregates with carbon nanotubes, amorphous carbon and impurities (Figure 1) that should be broken before flotation. 4) Water-soluble reagents should be used. Collectors and foaming agents mostly form emulsions with sufficiently large dimensions, compared to the particles to be extracted, a "reagent-nanoparticle" conglomerate, removed into the foam product, is formed that has to be cleaned of the collector and foaming agent. 5) Size of the gas bubbles for this flotation should be commensurate with the size of the particles to be floated, this will prevent the mechanical removal of particles into the foam product. 6) The hydrophobic component of flotation, air bubbles, are quickly expelled from water. In the usual flotation, a lot of bubbles of different sizes are created, entropy increases in the local volume, bubbles coalesce and float. To reduce the entropy of this local system to the necessary time interval for flotation, it is needed to disperse bubbles when they are introduced into a flotation machine, and it is important to achieve smaller bubbles with a narrow size distribution function. 7) Concentration of blowing agents, superficially active substances (SASs) and nanoparticles themselves can act as a regulator of bubble sizes. 8) Sorption rate for SASs and nanoparticles at the gas-liquid interface varies significantly. 9) Coating of hydrophobic particles, parts of particles with small gas bubbles will contribute to an elementary act of flotation that is coalescence of larger bubbles with small bubbles. Best option for flotation of nanoparticles is the initial formation of bubbles on their surface and the gradual increase of these bubbles due to the gas dissolved in the pulp.

Conducted experiments in a 3-chamber flotation machine (Figure 2) made it possible to create a foam layer, more than 15 cm, as a result, in a foam product, carbon content was from 96 to 97% for a number of flotation experiments, and for silicon – from 1.3 to 1.7 %. At the same time, the content of silica in the flotation tail was in the range from 96 to 97%, and carbon – from 1.5 to 2.5%. Observing all the conditions for the flotation process in the 3-chamber flotation machine, stable results for obtaining 2 new products were received: a foam one with a carbon content of about 97%, and a flotation one with a content of silica of more than 98%. Foam product is a black suspension. Elemental composition, predominantly, consists of carbon (95-97%), amorphous carbon, silicon carbide, unreacted graphite anode residues, carbon nanotubes. Structurally, it includes both large particles of an indefinite shape and long filaments, balls of nanotubes (Figure 2a). The flotation tail is 98% of amorphous microsilica of a spherical shape (Figure 2b). Particle sizes of the obtained product vary from 0.01 μm to 1.3 μm with a maximum particle distribution of about 0.1 μm (data obtained using a laser particle size analyzer ANALYSETTE 22 NanoTec from FRITSCH).
Figure 1. Conglomerates of carbon nanotubes and non-carbon particles, including SiO2.

Figure 2. Obtained ultradispersed materials (unrefined): a - foam product (conglomerates of carbon nanotubes), b - flotation tail (nano silica granules).

The optimal technological regimes for obtaining new products were determined: preliminary conditioning (conditioning time from 0.5 hours to 1.5 hours) of wet slime (about 10 kg) with kerosene (2.5 mg per 1 dm³ of pulp) and pine oil (100 mg per 1 dm³ of pulp) in the cavitator at pH = 8.5. Flotation was carried out in a developed 3-chamber flotation machine with a volume of 20 dm³ for 30 minutes with the help of an air-hydraulic aerator with air sucking from the atmosphere. Pulp is, thus, pumped by means of a pump at a pressure of 0.4 MPa from the I purification chamber to the aerator. This technique for obtaining new materials involves the subsequent purification of the foam product from silica residues by etching in hydrofluoric acid, by annealing at a temperature above 600 °C. After further processing, new ultrafine materials look as follows (Fig. 3a, b).

Obtained new materials, Figure 3, are interesting in that recently much attention has been paid to the problems of exogenous modification of alloys with nanoscale powder materials. Exogenous nanomodification (NM) involves the introduction of specially prepared powders that consist of refractory particles of size less than 100 µm into the melt. Herewith, a clad (adsorption) layer should provide not only good wettability of the particles, but also their resistance to melting and dissolution in the modifying alloy. Analysis of such process, conducted under the condition of interaction of the melt with the adsorbed layer on a flat substrate, showed [3,4] that for metals with a melting temperature of 1000-2000 K, stability of such complex can persist at significant overheating [5,6]. Possessing high wettability, such particles are homogeneously distributed in the bulk of the liquid metal and become crystallization centers during the cooling of the melt [5,6]. As a result, structural components of the
alloy are ground that, in turn, affects the properties of the solidified metal. There are numerous studies of the influence of this method of modification on the structure and properties of castings from heat-resistant nickel alloys, alloys based on iron, aluminum, etc. [5.6].

Figure 3. Finished ultradispersed materials after aftertreatment, a – foam product (conglomerates of carbon nanotubes), b – Flotation tail (silica nano-granules) from the carbon shell.

4. Conclusion
1. Two new nanoscale materials from silicon wastes were developed. Carbon material consists of a mixture of amorphous nanoparticles with a maximum size distribution of 200-500 nm, aggregated coils of carbon nanotubes about 1% of the volume, globular nanoparticles of a spherical form of crystalline silicon dioxide with a maximum size of 200-300 nm, coated with a carbon shell with a wall thickness of 4-6 nm. Silicate material contains over 90-97% of amorphous silicon dioxide with a maximum size of 200-300 nm, and also contains silicate nanotubes representing silica with a diameter of 50-60 nm.

2. It was determined that the mechanism for the modification of metals and alloys, obtained by nanostructured materials, is formed in accordance with the hypothesis of a local stress field at the ends of the tubes, increasing the rate of formation of the crystallization centers of the melt. An additional modifying effect is exerted by the large surface energy of nanostructured materials, if we compare them with modifying materials that have micron-sized structures.

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