The application of copper-containing nanoparticles as a gas nitriding catalyst

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Abstract. The results of the study of the possibilities of using copper-containing nanoparticles obtained by pseudomatrix synthesis as a catalyst for cyclic gas nitriding of steel products were presented in this paper. It was shown by the example of steel 08Yu (corresponding to the European standard of steel DC04/DC03 EN 10139) that the preliminary application of nanocomposite-catalyst including copper-containing nanoparticles and macromolecules of poly-(N-vinylpyrrolidone) polymer pseudomatrix to the product significantly intensified the chemical heat treatment process. It was found that under identical treatment process conditions the thickness of the diffusion layer for a sample with a pre-applied nanocomposite was 90 µm, and without such pretreatment — 42 µm. It is noted that the achievement of this effect is due to the catalyst synthesis peculiarities, which allows to obtain a copper sol with a narrow size distribution of particles resistant to aggregation.

1. Introduction
The currently proposed intensification methods of the steel treatment process have a few disadvantages: delayed nitrogen diffusion during the process of saturation through the surface layer leading to an increase in the duration of the process, the formation of the insufficient layer thickness of metal-ceramics on the surface of products, the non-equilibrium structures formation with high microhardness [1, 2]. However, the proposed methods are characterized by high cost and strict requirements for the application and manufacture.

In this matter, a study aimed at improving the steel surface process hardening productivity, due to the intensification of the diffusion nitriding process is relevant.

Various options have been proposed as catalysts for the nitriding process, for example: solids, liquids and gases [3, 4]. It was found that accelerators do not affect the hardness and depth of the layer, since they only change the composition of the gas phase and do not change the value of the nitrogen diffusion coefficient.

The use of copper as a nitriding catalyst was also described in the literature [5]. The thickness unevenness of the copper deposited by the galvanic method, especially on products profile complex is main disadvantages. This leads to lose of film catalytic properties and does not allow to receive a monolithic zone of metal ceramics in the diffusive nitrided layer.

The obtaining of copper nanoparticles by reducing Cu^{2+} ions in aqueous solutions of polymers used as regulators of the size resulting nanoparticles, as well as the possibility of controlling the size of synthesized copper-containing nanoparticles was investigated in our early works [6-8]. The sol nanocomposite obtained and used by us as a catalyst for nitriding allows to eliminate the above disadvantages, due to the nanoscale range and optimally selected components. This article focuses on
the preparation and evaluation of the influence of copper nanoparticles on the diffusion processes of nitriding.

2. Experimental

Copper(II) sulfate pentahydrate (reagent grade, Reakhim, Russia), tert-butyamine borane (TBAB) (98% Aviabor, Russia), poly(N-vinylpyrrolidone (PVP) (Fluka, Mn = 3.6×10^5) and hydrochloric acid (reagent grade, Reakhim Russia) were used without further purification. Solutions were prepared in twice distilled water. Low-alloy steel 08Yu was used (GOST – state standard of the Russian Federation - 9045-93, corresponding to the European standard of steel DC04/DC03 EN 10139) as an object of chemical and heat treatment.

The sizes and morphology of metal nanoparticles were studied using transmission electron microscopy (TEM). Studies were carried out on LEO 912 AB OMEGA microscope (“Carl Zeiss”, Germany).

When preparing samples, a drop of sol was applied on a copper grid covered by formvar and the excess liquid was removed by filter paper. The sample was dried at room temperature (drying time did not exceed 5-10 minutes).

The morphology of the samples after heating was examined using scanning electron microscopy (SEM). SEM images were measured on a Versa 3D DualBeam scanning electron/focused ion beam microscope (FEI, USA) equipped with energy dispersive X-ray spectroscopy system (EDAX, USA) in high vacuum mode using a backscattered electron detector.

Processing of micrographs was carried out by software Gatan Digital Micrograph (Gatan, USA) and ImageJ (NIH, USA).

The durometric analysis of the microhardness distribution over the nitrided layer thickness of samples was carried out on a microhardness tester PMT-3 (Lomo, Russia).

Metallographic studies were carried out using a light microscope "AXIOVERT 25CA"(Carl Zeiss, Germany). Marble reagent (4 g CuSO_4 + 20 ml HCl + 20 ml H_2O) was used to identify the structure.

At the first stage of the experiment, the reduction reaction of copper ions TBAB at room temperature in air was used to obtain copper-containing nanoparticles. TBAB (0.01 – 0.03 mol/l) was added to an aqueous solution containing copper salt (0.01 mol/l) and PVP (0.01 mol/l).

At the second stage of the experiment, the resulting composite system was applied to the surface of 08Yu steel product. The steel sample was maintained in the sol of copper-containing nanoparticles for 2-3 minutes at room temperature. Further, the steel product was dried at room temperature with air flow.

At the third stage, the steel sample was exposed to chemical heat treatment. At the beginning, it was placed in a sealed container, heated in an atmosphere of ammonia and carbon dioxide with the volume ratio of 1:1 to the temperature of 575 °C. Then, the nitriding was performed under isothermal exposure at the same temperature. At the same time, the cyclic change of the gas mixture was carried out: in the first stage of the cycle, a mixture of ammonia and water vapor was used, in the second stage — a mixture of ammonia and carbon dioxide. The amount of ammonia during saturation was kept constant and equal the volume ratio of 1:1 to the volume of the other saturating atmosphere component in the first and second stages.

After 3 hours from the beginning of the nitriding process, the sample was cooled with the furnace in an ammonia atmosphere to a temperature of about 200 °C and unloaded from the furnace reactor.

The chemical heat treatment of steel 08Yu sample was carried out by described method (the third stage of the experiment) without application of nanocomposite to estimate the effectiveness of the catalytic system.

3. Results and discussion

The formation of copper sol is occurred as a result of copper ions reduction by TBAB in an aqueous solution of CuSO_4 and poly(N-vinylpyrrolidone). The color of the reaction mixture changes during the reduction process: without the reducing agent – blue, after addition of TBAB becomes yellow, then
yellow-orange, and then lilac. The color change of the reaction mixture indicates the formation of Cu$^{2+}$ ion reduction products.

The obtained nanocomposite is a complex of copper-containing nanoparticles with the polymer pseudomatrix macromolecules, which is PVP. Polymer macromolecules shield particles, preventing their aggregation. Figure 1 depicts the TEM image of the obtained sol of nanocomposite.

![Figure 1. TEM image of particles in the Cu sol obtained by the reduction of copper ions in solution of PVP.](image1)

The theory of pseudomatrix (pseudotemplate) synthesis of similar sols which is based on the concepts of the cooperative character of noncovalent interactions of macromolecules with the nanoparticles surface makes it possible to effectively control the dimensional characteristics of nanoparticles in the processes of synthesis of sols [9,10] The particle numerical size distribution histogram is presented on figure 2. The particle size distribution is narrow. The main fraction of sol particles diameters is in the range of 4-12 nm.

![Figure 2. Histogram of numerical size distribution of particles in the Cu sol obtained by the reduction of copper ions in solution of PVP.](image2)
Upon the exposure of nanocomposite coated steel products at the temperature of 575 °C (in a flowing atmosphere of ammonia and water vapor mixture) metallic copper is oxidized to CuO, which then acts as a catalyst for ammonia dissociation. The formation of copper oxides from copper-containing nanoparticles is provided by the supply of water vapor at the first stage of the nitriding cycle. At the second stage of the cycle, copper oxides are reduced to pure copper by hydrogen formed as a result of ammonia dissociation.

A diffusion layer thickness of 90 µm (figure 3) was obtained as a result of chemical heat treatment of the nanocomposite coated steel 08Yu sample. Under the standard method of nitriding under similar conditions, the layer thickness was 42 µm (figure 4). The microhardness levels in both cases were the same.

![Figure 3. Microstructure of the steel 08Yu sample pre-coated by nanocomposite after chemical heat treatment.](image)

![Figure 4. Microstructure of the steel 08Yu sample after chemical heat treatment without application of copper-containing nanocomposite.](image)

Studies have shown that copper-containing nanoparticles deposited on the surface as part of the composite coating exhibit high catalytic activity, which allows to obtain an additional effect in the reaction of ammonia dissociation with the generation of nitrogen ions, and also lead to a significant increase in the number of active centers through which nitrogen penetrates into the steel. This is facilitated by the fact that the particles do not aggregate when heated, but are distributed over the surface at a distance from each other, thereby accelerating the diffusion of nitrogen ions into steel products in high concentration. Figure 5 depicts the micrograph of the sample after heating up to 1000 °C.
4. Conclusion
The results of a study confirming the possibility of using copper-containing nanoparticles to improve the efficiency of the chemical heat treatment process of steel were described in the article. It was found that the Cu-containing nanoparticles used as a nitriding catalyst are able to influence the rate of ammonia dissociation reaction. The use of copper-containing nanoparticles as a catalyst for gas nitriding allows to intensify the process, as well as to obtain a uniform hardened layer on the steel surface with a monolithic zone of cermets.

The efficiency of the resulting catalyst is due to the peculiarities of synthesis. Using of polymer protector PVP provides a narrow particle size distribution in the range of 4-12 nm and the absence of their aggregation at the initial stage (during synthesis) and subsequent (during heating).

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![Figure 5. SEM image of particles in the sample after heating up to 1000 °C.](image-url)
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