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NANOMATERIALS

ON THE PROPERTIES OF A STEEL MODIFIED WITH CARBON NANOMATERIALS

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Results of investigation of the surface of a steel modified with carbon nanomaterials having different contents of carbon nanostructures by the method of atomic-force microscopy are presented. Experiments on the microhardness of this steel have been carried out and the thickness of its modified layer was determined.

Keywords: *carbon nanomaterials, nanotubes, nanofibres, steel, thermal treatment, atomic-force microscopy, microhardness.*

Introduction. Nanostructure materials based on carbon nanofibres and nanotubes occupy a significant place in composite-material science [1, 2]. It has been established that polymers [3] and metals pigmented with carbon nanostructures have a high strength. However, the mechanism of influence of the indicated structures on the strength properties of nanomaterials is not clearly understood.

Formulation of the Problem. The aim of the present work is to determine the influence of the appication of carbon nanomaterials containing carbon nanotubes and nanofibres to the surface of a steel on the structure of this surface and the microhardness of its modified layer.

Object of Investigation. Carbon nanomaterials were obtained via interaction of a carbon-containing gas mixture with the plasma of a high-voltage atmospheric-pressure discharge on a setup described in detail in [4]. A mixture of methane with air was used as the initial material. This mixture was fed into a plasma-chemical reactor where it was transferred through the zone of a high-voltage electric discharge. The voltage across the electrodes of the discharge gap was 2.4 kV and the discharge current was equal to 100 mA. The composition of the mixture was somewhat larger than that required for the completion of a partial oxidation reaction. After this reaction was completed, a mixture consisting mainly of nitrogen, hydrogen, carbon oxide, and the undecomposed part of the hydrocarbon was formed. This part interacting with the hot metal of the reactor wall formed carbon nanostructures. The temperature of the growth surface of these structures was 650–950^{o}C depending on the experimental conditions and the distance of the growth zone from the plasma flow. A part of the hydrocarbons was subjected to pyrolysis, leading to the formation of soot particles that were carried away then with the reaction products. After each experiment, the carbon nanomaterial was gathered from the walls for further use.

The carbon nanomaterial obtained represented a black powder of bulk density of 0.21 g/cm^3 containing as much as 40–50% of structurized carbon and as much as 30% of amorphous carbon. The remaining part comprised graphite (~15%) and particles of metals and their oxides (~5%). The material containing nanostructures was subjected to a special acid and thermal treatment for removal of amorphous carbon and metal particles. After the purification of this material, the content of structurized carbon in it reached 70–80%.

Figure 1 shows electronic photographs of samples of the carbon nanomaterial obtained; they were made with the use of a scanning-electron microscope and a transmission-electron microscope.

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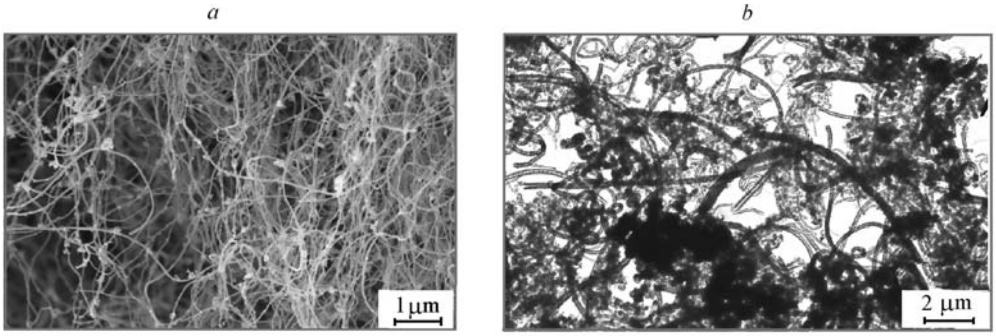

Fig. 1. Photographs of a carbon nanomaterial obtained on a scanning microscope (a) and a transmission electron microscope (b).

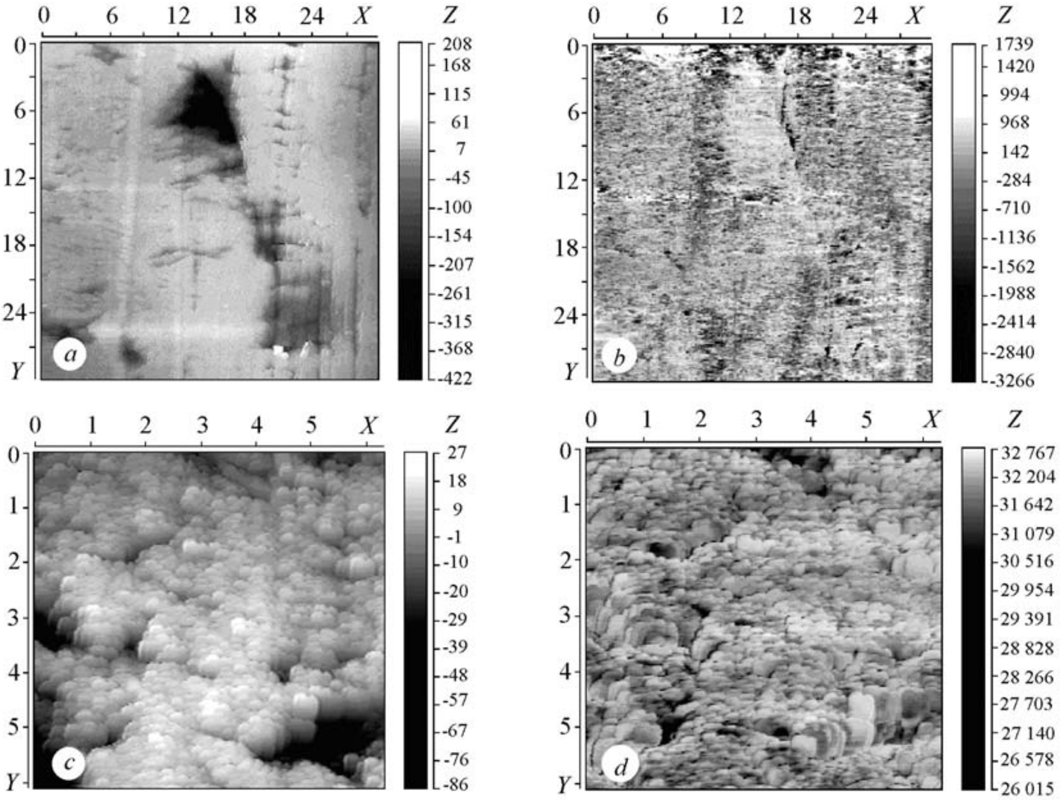

Fig. 2. AFM images of a steel substrate: a, c) topography (regions 30 × 30 and 6 × 6 μm); b, d) lateral forces (regions 30 × 30 and 6 × 6 μm). *X*, *Y*, μm; *Z*, nm (topography); *Z*, arb. units (lateral forces).

As the test samples we used four metal plates of stainless Kh18N10T steel of size 10 × 10 mm: 1) a plate to the surface of which a layer of a carbon nanomaterial with a structurized-carbon content of 60–70% was applied; 2) a plate to the surface of which a thin layer of a carbon black with a structurized-carbon content of up to 5% was applied; 3) a plate free of carbon-nanomaterial layer that was subjected to subsequent treatment; 4) an initial steel sample that was not subjected to subsequent treatment. The average thickness of the carbon-nanomaterial layer applied to the surface of samples 1 and 2 was 0.216 and 0.215 mm respectively (its density ρ was approximately 0.22 g/cm^3 = $0.22 \cdot 10^{-3}$ g/mm^3).

Samples 1–3 were placed on a quartz plate and were covered by an identical quartz plate from above, and the joint between the plates was filled up with a high-temperature sealant. Than the samples were subjected to thermal treatment for 15 min at a temperature of 800$^{\text{o}}$C in a muffle furnace.

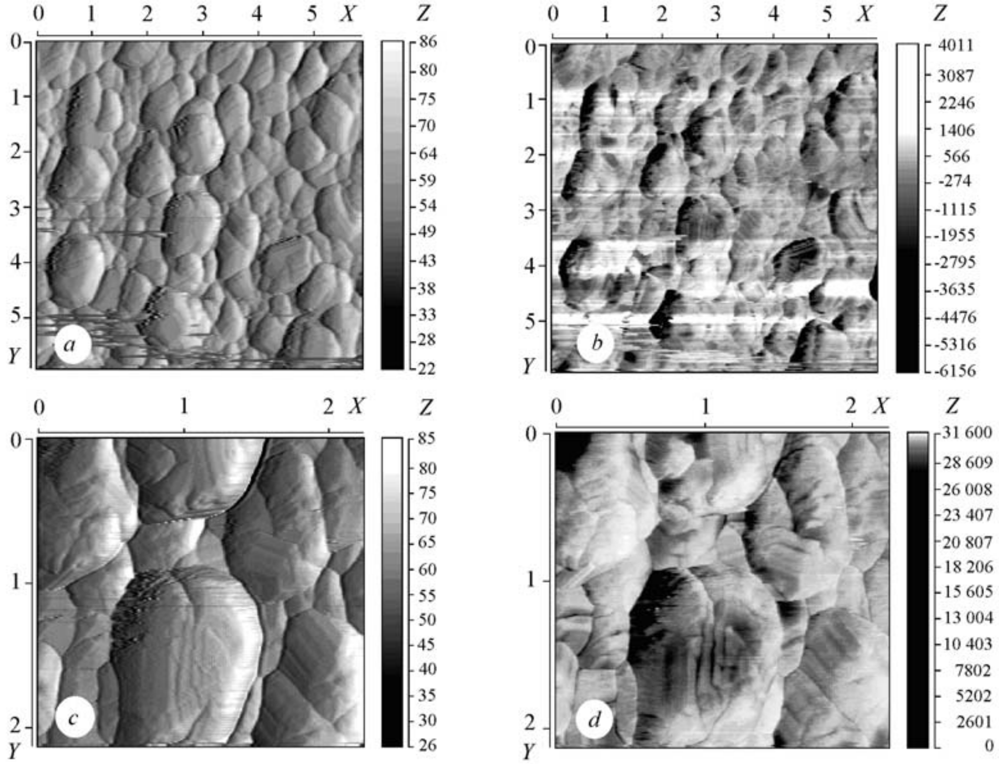

Fig. 3. Surface of the steel (sample 3) after the thermal treatment: a, c) topography (regions 6 × 6 and 2 × 2 μm); b, d) lateral forces (regions 6 × 6 and 2 × 2 μm). *X*, *Y*, μm; *Z*, nm (topography); *Z*, arb. units (lateral forces).

Results of Investigation. The investigations were carried out on an atomic-force microscope in the contact regime with the use of CSC12 probes with a cantilever of stiffness 1 N/m. The topography of the surface of the plates being investigated and the lateral forces acted on it were photographed.

On the initial steel surfaces, oriented traces of the mechanical treatment (rolling) of the metal sheet were detected (Fig. 2a and b). The roof-mean-square deviation of the surface roughness was 54 nm in the region of size 30 × 30 μm. The image of the lateral forces shows the surface inhomogeneity manifesting itself as the waves transverse to the rolling direction. An investigation with an increased resolving power (a scanning of the regions of size 6 × 6 μm) revealed the grain structure of the surface layers of the material (Fig. 2c and d). The characteristic size of the grains was 60 × 150 nm, and they were oriented crosswise to the rolling direction.

A further detailing in the process of scanning did not allow us to detect other features in the structure of the steel. An investigation of the influence of the thermal treatment of the steel samples (heating to 800°C with subsequent cooling) has shown that, in this case, the structure of the surface layers of the steel changes substantially (Fig. 3).

As the sizes of grains increased (300–900 nm), their form became more isotropic and the texture of the grains took the form of twinning lines representing the planes of their growth in the process of recrystallization of the steel surface.

The inclusion of the carbon nanomaterials in the process of recrystallization of the steel plates substantially changed the structure of their surface. When a carbon nanomaterial with a low content of structurized carbon (lower than 5%) was applied to the surface of the steel plate, the size of the grains on this surface was decreased to 200–400 nm (Fig. 4). In this case, the grains retained their own structure with traces of the growth planes. The existence of grains with substantially different contrasts appeared on the images of the lateral forces points to the fact that the materials contained in the surface layer of the steel are different in phase. It is conceivable that this is due to the growth of the carbide phase of the iron, which cause the hardness of the material to increase.

The application of the carbon nanomaterials with a high content of structurized carbon (as high as 70%) on the surface of a steel plate before the thermal treatment of this plate led to a substantial "grinding" of the structure of

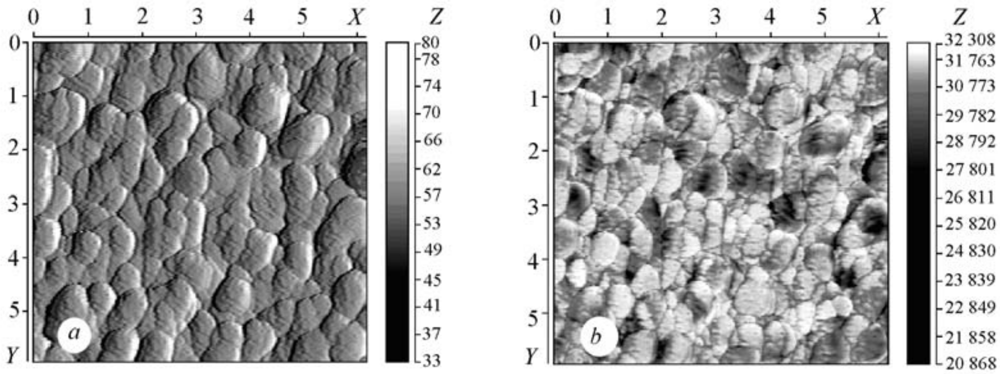

Fig. 4. Surface of the steel recrystallized in the presence of the carbon nanomaterial with a low content (lower than 5%) of structurized carbon (sample 2): a) topography; b) lateral forces (region 6 × 6 μm). *X*, *Y*, μm; *Z*, nm (topography); *Z*, arb. units (lateral forces).

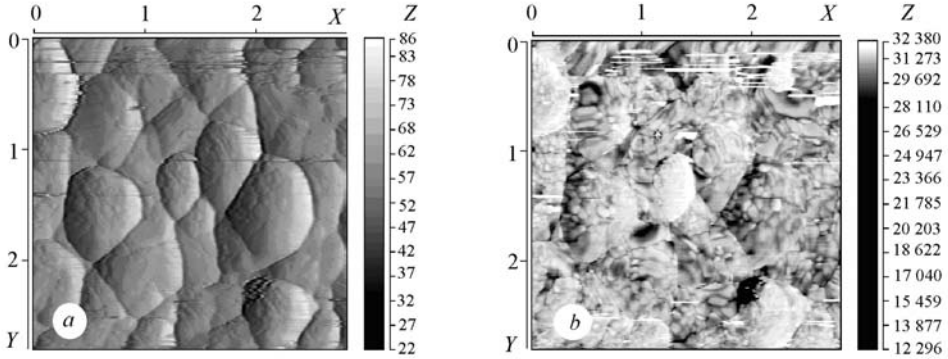

Fig. 5. Surface of the steel recrystallized in the presence of the carbon nanomaterial with a high content of structurized carbon (sample 1): a) topography; b) lateral forces (region 3 × 3 μm). *X*, *Y*, μm; *Z*, nm (topography); *Z*, arb. units (lateral forces).

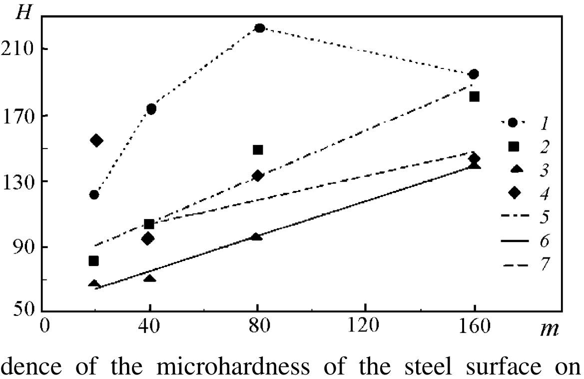

Fig. 6. Dependence of the microhardness of the steel surface on the load on the indenter: a) sample 1; 2) sample 2; 3) sample 3; 4) sample 4; 5, 6, 7) linear dependences for samples 2, 3, and 4 respectively. *H*, hardness units; *m*, g.

the surface layer of the steel in the process of its recrystallization (Fig. 5). A two-level structure is seen on the AFM images of the surface region 3 × 3 μm of a steel plate: grains-embedments of nanometer size (20–30 nm) are positioned on the micrograins of size ~1 μm.

The samples were tested for microhardness at the Department of Micro- and Nanostructure Investigations of the Scientific-Research Center of Problems on Resource Conservation of the National Academy of Sciences of Belarus.

The investigations were carried out at loads of 20–160 g during 10 sec with the use of a PMT-3M microhardness meter by the Vickers method. The length of the diagonals of an indentation was measured with the use of a screw eye-piece MOV-1-16 microscope in the dark field.

Figure 6 shows the experimental dependence of the microhardness of the coating of steel plates on the load on the indenter. The data obtained show that the microhardness of all the samples increased with increase in the load. The corresponding dependences are practically linear everywhere, excepting the first point in the steel sample 4. The data obtained for sample 1 show that the microhardness of its surface increases sharply to a maximum, and then it decreases somewhat. The microhardness values for samples 2 and 3 differed by no more than 25% from the analogous values obtained for sample 4 that was not subjected to treatment, while the microhardness values obtained for sample 1 were larger by almost two times than the microhardness of the control sample.

An analysis of the data obtained, carried out with the use of the indentation-depth scale, has shown that the increase in the microhardness of sample 1 is evidence of an increase in the thickness of the modified layer, which was ~4 μm in our experiments.

Conclusions. The inclusion of a carbon nanomaterial with a high content of a structurized carbon into he surface layers of a steel in the process of its treatment causes a change in the structure of these layers due to the formation of nanograins in them and a marked increase in the microhardness of the material; this effect is attained in the case where the thickness of the modified layer does not exceed 4 μm. An AFM analysis of the surfaces of the steel plates investigated revealed a pronounced difference between the regimes of the lateral forces in them, which points to the difference betwwen the phases of the material at the nanolevel. It is necessary to further investigate the recrystallization of steel in the presence of carbon nanomaterials and as well as physical and mechanical properties of its surface layer formed in this case for determining the mechanisms of restructurization of the surfaces of metals as a result of the formation of a nanostructure layer on them and for optimization of the technological regimes of this modification.

NOTATION

H, microhardness, hardness units; m, mass of the load on the indenter, g; X, Y, coordinates, μm; Z, coordinate, nm (topography), arb. units (lateral forces); ρ, density, g/cm^3.

REFERENCES

1. E. Fitzer (Ed.), *Carbon Fibres and Their Composites*, Springer-Verlag, Berlin (1986).
2. P. J. F. Harris (Ed.), *Carbon Nanotubes and Related Structures*, Cambridge University Press, Cambridge (1999).
3. S. S. Pesetskii, S. A. Zhdanok, I. F. Buyakov, S. P. Bogdanovich, A. P. Solntsev, and A. V. Krauklis, On the structure and properties of polyamide 6 modified in a melt by carbon nanomaterials, *Dokl. Nats. Akad. Nauk Belarusi*, **44**, No. 6, 102–107 (2004).
4. S. A. Zhdanok, A. V. Krauklis, I. F. Buyakov, P. P. Samtsov, and K. O. Borisevich, Formation of carbon nanostructures in the decomposition of methane in the plasma of a high-voltage atmospheric-pressure discharge, *Inzh.-Fiz. Zh.*, **81**, No. 4, 617–620 (2008).