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Preparation of the Iron Carbide–Fullerene Black Nanostructured Composite Coating on the Steel-45 Surface

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Abstract—Fullerene black at 1150ºC interacts with the surface of iron to form a nanostructured composite coating consisting of orthorhombic iron carbide crystallites of 60–100 nm size and dispersed islands of fullerene black. In the process of formation of the composite coatings both the fullerene black with a particle size of 40–50 nm and the carbon oxide formed in the process were involved. Under the conditions of the process, the content of hydrogen and oxygen in the structure of fullerene black decreased, straightening out curved surfaces occurred, and appeared a system of aromatic conjugation.

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Recently the interest in functional carbon-based nanomaterials has increased that often show some unusual properties. Much of this interest is caused by the fact that these materials are nano-sized that makes them closer to the molecular (pseudomolecular) materials both by the size and properties. The possibility of obtaining hybrid materials based on carbon nanomaterials with graphene structures (nanotubes and nanofibres) largely is hampered by their chemical inertness due to the presence of a stable aromatic structure. The use of fullerenes for these purposes as reactive nano-objects is complicated by their solubility and sublimation (vapor pressure at 530°C close to 760 Torr).

However, by ball milling of fullerene [60] with iron powder composites were obtained comprising iron carbide and having high hardness [1–4]. Composites with similar properties were also obtained using carbon black [5, 6] or graphite [4]. It was reported [7] on obtaining dispersed particles of iron carbide by treatment of a mixture of iron oxide, carbon black, and aldehyde. Dispersed phase of η-Fe_3C according to [8] can be prepared by the interaction of the metal with an active carbon oxide formed at the thermal treatment of a mixture of aluminum oxide, carbonate or hydrogen carbonate, and granular graphite. According to [9] the formation of iron carbide was achieved using as a reducing agent the carbon black, which has specific properties. The hardening of the surface of drilling tool can be achieved by fusing a mixture of carbide material (various forms of tungsten carbide), and a matrix that includes iron, nickel and cobalt or their alloys, and 0.05 wt % of the fullerene material (spherical, elliptical or nanotubes or a mixture thereof) [10]. The nanoparticles of carbides of titanium, niobium, and tantalum were obtained at the interaction of the respective metal powder, multiwall nanotubes, and iodine (10:10:1 mol) at 1000–1100°C over 168–215 h [11]. In this study, we attempted to obtain iron carbide on the surface and thus to achieve the steel 45 surface hardening using fullerene black as a nano-sized object. As has been shown earlier [12], fullerene black added to a lubricant promotes the formation of wear-resistant surface layers of materials of friction couples.

Fullerene black is insoluble residue after extraction of fullerenes from the condensed product of electric-arc evaporation of graphite, the by-product at producing fullerenes. The fullerene black yield is by an

order of magnitude greater than the yield of fullerenes. Being the unclosed analog of fullerene, the fullerene black is electron-deficient nonconjugated alkene and its reactivity is increased compared to the fullerenes. However, in contrast to the fullerene, it is insoluble in any solvents and is not sublimated. According to chemical analysis, fullerene black contains, besides carbon, 1.2 wt % of hydrogen and 7.4% of oxygen (ratio H/O ≈ 2.6:1 mol.). Surface layers of fullerene black, according to XPS, are enriched with oxygen and contain 91.0 at. % of carbon and 8.8% of oxygen.

At thermal desorption, which occurs in a wide temperature range 100–700ºC, fullerene black liberates mainly oxygen (*m/e* 32), water (*m/e* 18, *m/e* 17, *m/e* 1) and carbon oxides, predominantly CO (*m/e* 28, Fig. 1). Such a wide range of thermal decomposition of fullerene black is not associated with the dynamics of the thermal analysis (rate of temperature rise 10º per 1 min) because the mass loss at the same temperatures in a dynamic and isothermal (60 min) modes are virtually identical. The presence of water in the products of thermolysis is not consistent with the calculated according to the data of analysis: analysis gives the H/O molar ratio greater than 2.

The presence of CO in the products of thermolysis, the small size of particles (40–50 nm), the high reactivity, and the absence of sublimation define the use of fullerene black for the obtaining iron carbide. Typical carburizers for the formation of carbon monoxide used at the producing metal carbides (e.g., carburizer charcoal according to GOST 2407-83, carburizer semi-coke by GOST 5535-76) contain up to 30 wt % of carbonates of the elements of I and II groups.

Indeed, iron reacts with fullerene black (10 wt %) to form carbide, the respective *endo* effect is observed at 1143ºC (Fig. 2). At the interaction of iron(III) oxide with fullerene black (20 wt %) the oxide is reduced to the metal at 620–635ºC and then occurs formation of iron carbide with the similar *endo* effect at 1144ºC (Fig. 3). Formation of iron carbide and reduction of iron oxide under the influence of fullerene black confirms the possibility of its use as a component for prodicing carbide both in the blast furnace process and at the surface hardening of carbon steels.

We confirmed this assumption by carrying out interaction of fullerene with the surface of iron. As a result of interaction with the fullerene black, on the surface of steel 45, as seen from the scanning electron microscopy (SEM) images (Fig. 4), a coating is formed. According to X-ray analysis the coating formed consists of orthorhombic iron carbide (Fig. 5).

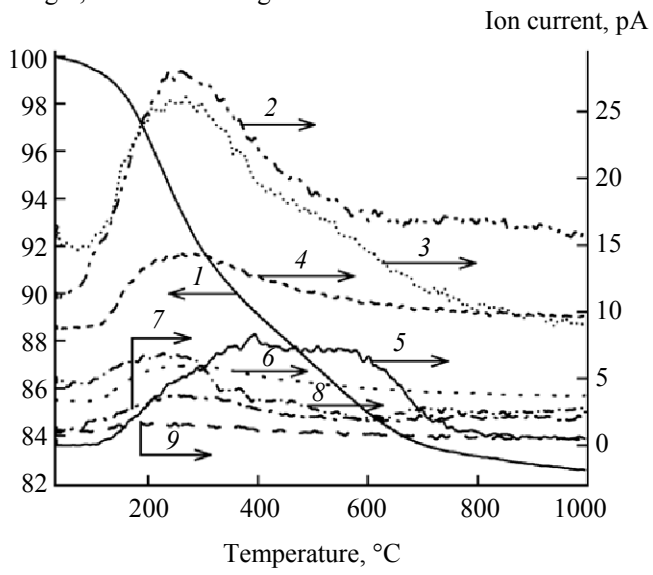

Fig. 1. (*1*) Thermogram of fullerene black in argon with mass spectral analysis of gaseous products with mass numbers (*2*) 18, (*3*) 28, (*4*) 2, (*5*) 44, (*6*) 1, (*7*) 17, (*8*) 32, and (*9*) 14. For convenience, the values of ionic currents for particles with *m/e* 2 are increased 10-fold.

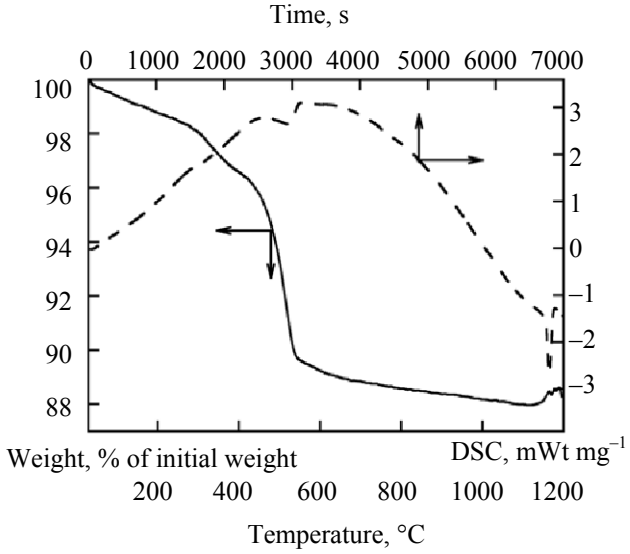

Fig. 2. Thermogram of iron–fullerene black composition in argon flow.

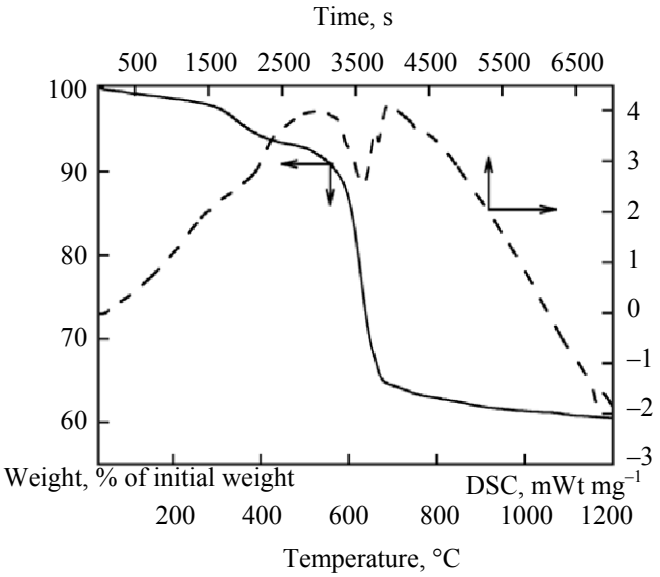

Fig. 3. Thermogram of the composition iron(III) oxide–fullerene black in argon flow.

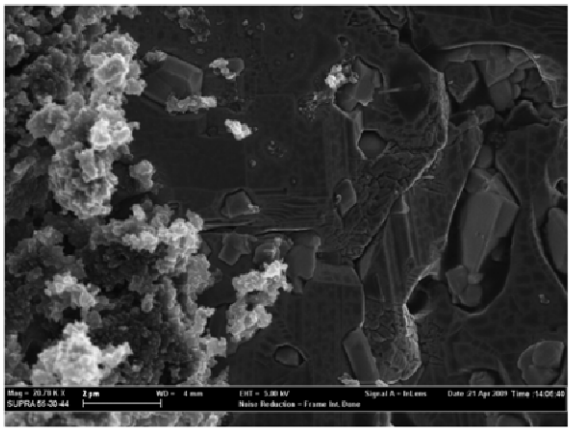

Fig. 4. The steel 45 surface image after interaction with the fullerene black obtained with scanning electron microscope.

Such carbide coating was not found on the surfaces of steel not contacted with the fullerene black that clearly points that the interaction includes a diffusion component. On the surface of a sample of 45 steel after interaction with the fullerene black we detected also the reflexes of the α-iron of original steel 45 (Figs. 5a, 5b).

The structure of the obtained carbide coating consists of equiaxed subgrains of 10–20 μm size, which in turn are composed of crystallites of 60–100 nm size (Fig. 4). These subgrains contain about 46 at % of Fe and 35 at % of carbon, which is satisfactorily consistent with the composition of iron carbide Fe_3C. Between the iron carbide subgrains the islands of fullerene black are located with a particle size 40–50 nm (Fig. 4). Indeed, these amorphous inclusions, according to the results of electron microscopy analysis, contain mainly carbon (more than 90 at %). By our estimation, the content of the fullerene black islands on the steel 45 surface does not exceed 5%. Due to the amorphous nature, the small particle size, and low content of fullerene black in the coating, its reflections cannot be detected in the diffractogram (Fig. 5). Thus, our results suggest that the interaction of fullerene black with 45 steel leads to the formation on the surface of the latter a composite nanostructured coating consisting of orthorhombic Fe_3C–fullerene black.

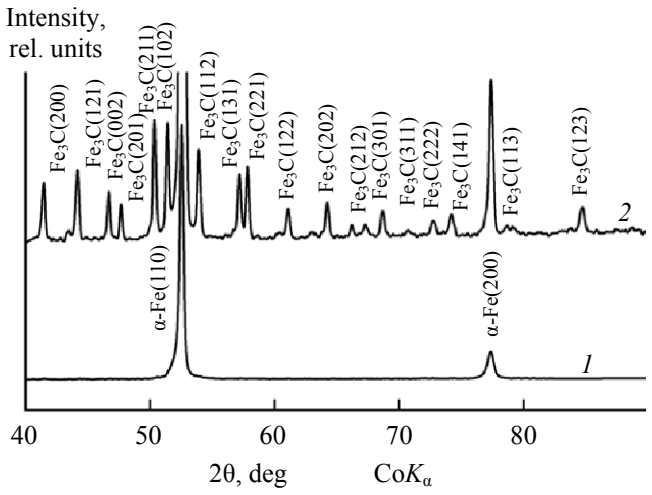

Fig. 5. Fragments of the diffractograms of the steel 45 surface (*1*) before and (*2*) after interaction with the fullerene black.

Microhardness of the carbide coating is 6520 MPa, whereas that of the original steel (annealed at about 400°C for 1 h) equals 3200 MPa, which confirms the significant effect of surface hardening of steel 45 as a result of its interaction with the fullerene black.

Formation of iron carbide Fe_3C at the contact of the iron or iron oxide particles with fullerene black, that has not been observed at the use of graphite, indicates a possibility to apply fullerene black for hardening the surface of one (or both) elements of a friction pair. The presence of fullerene black in the formed layer of iron carbide and the results of [12] allow to expect that,

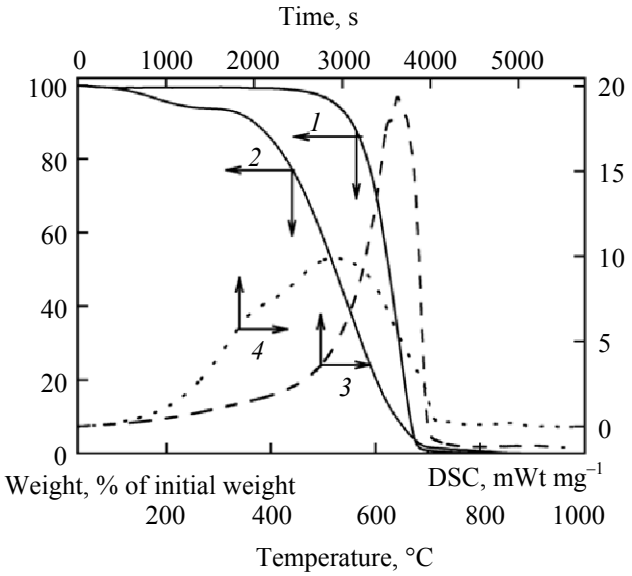

Fig. 6. Oxidation thermograms of fullerene black (*1, 3*) before and (*2, 4*) after interaction with a sample of steel 45.

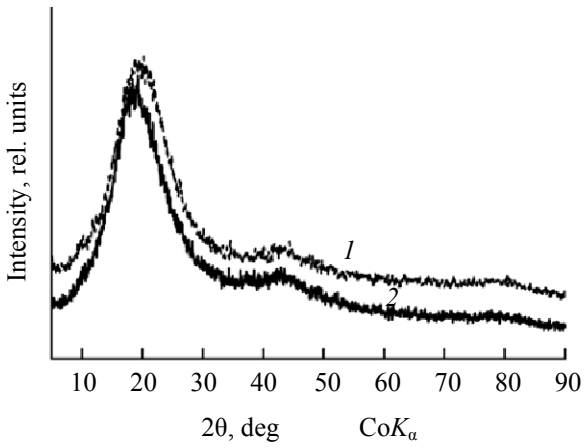

Fig. 7. Fullerene black diffraction pattern (*1*) after and (*2*) before interaction with the sample of steel 45.

along with a noticeable effect of hardening, the coating will have also improved antifriction properties.

After the interaction with the steel surface at 1150°C, the fullerene black becomes more resistant to oxidation (Fig. 6, *2, 4*), due to the flattening of curved surfaces in its structure and the appearance of the aromatic system of conjugation [13, 14]. Changes in the phase composition of the fullerene black were not detected (Fig. 7), but after interaction the content of hydrogen and oxygen in the fullerene black drops to 0.56 and 1.23 wt %, respectively (ratio H/O ≈ 7.2:1 mol). The reduction in the oxygen content is due to the oxidation of the fullerene black to carbon monoxide CO, because the oxygen content (7.4 wt %) is in satisfactory agreement with the mass loss (~17.5%) at the thermolysis (Fig. 1) with the formation of CO (not CO_2).

The decrease in the oxygen content due to the formation of carbon monoxide (Fig. 1) and the absence of iron carbide on the surface when graphite is used not adsorbing oxygen and water from the atmosphere, demonstrate the important role of carbon monoxide in this seemingly solid-phase process. However, the fact that iron carbide and fullerene black islands occur only on the steel surface contacted with the fullerene black points to the diffusion of carbon in obtaining iron carbide in this way.

As a result of the studies it is found that fullerene black at 1150°C exhibits high reactivity at the contact with iron and forms on the steel 45 surface a nanostructured composite coating based on the orthorhombic iron carbide crystallites of 60–100 nm size. The carbide coating also contains the inclusions of unreacted with iron fullerene black with the particle size 40–50 nm whose content does not exceed 5%. The microhardness of the nanostructured carbide coating is 6520 MPa, while the microhardness of the original steel 45 does not exceed 3200 MPa. In the interaction of the steel 45 surface with fullerene black leading to the formation of composite coating consisting of orthorhombic iron carbide crystallites of 60–100 nm size and fullerene black the fullerene black particles of 40–50 nm size are involved and carbon monoxide is released during the thermal treatment. The fullerene black phase composition suffers no changes at the thermal treatment, but both oxygen and hydrogen content in its structure decreases, the flattening of curved surfaces occurs and a system of aromatic conjugation appears.

EXPERIMENTAL

Fullerene black was obtained as insoluble residue after extraction of fullerenes from fullerene soot obtained according to [15]. Original steel 45 contains, besides the main component (iron), the following additives (wt %): Si 0.23, Cr 0.23, carbon 0.43, manganese 0.62.

The compositions iron–fullerene black and iron(III) oxide–fullerene black were prepared at mixing the

components (iron carbonyl or iron(III) oxide and fullerene black) by ball milling in an argon atmosphere. For obtaining the iron carbide on the surface, the 10 mm in diameter and 10 mm in height rod samples with polished faces were placed in a quartz ampule on a layer of fullerene black, the ampule was then evacuated and sealed. The ampule was heated to 1150ºC, maintained at this temperature for 0.5 h, cooled, and opened.

Elemental analysis was performed on a CHNSO elemental analyzer Vario Micro cube (Elementar Analysensysteme GmbH, Germany). Thermograms were recorded on a thermoanalyzer STA-409 PC Luxx coupled with a mass spectrometer QMS-403 C (NETZSCH, Germany). All the values of the mass numbers *m/e* are shown in atomic mass units.

Diffraction patterns were recorded on a DRON-3 instrument. The transmission electron microscopy measurements were made on a JEOL JEM-2000EX instrument, accelerating voltage 500 kV. The scanning electron microscopy measurements were performed on a Zeiss Leo Supra 25 scanning electron microscope.

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